

Fluorescence nanoscopy unveils the black box of industrial zeolite catalysts: Mechanisms and optimization of mass transfer-acidity-coke formation

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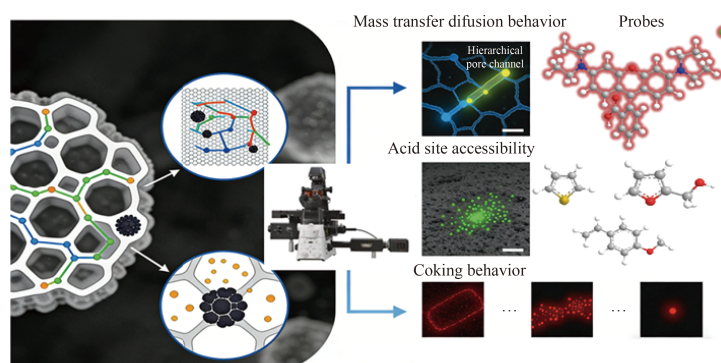
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Abstract: The performance of industrial zeolite catalysts, typically exemplified by fluid catalytic cracking (FCC) catalysts, is governed by microscopic behaviors such as mass transfer, acidity and coking. Conventional characterization techniques exhibit limitations in elucidating the structure-performance relationships. So, recent advances in super-resolution fluorescence imaging for deciphering the key microscopic processes are systematically summarized in this review:

(1) Mass transfer diffusion behavior: the heterogeneous diffusion of reactant molecules within hierarchical pore networks are revealed; (2) Acid site accessibility: nanoscale localization of acid sites and visualization of their accessibility are achieved; (3) Coking behavior: the spatiotemporal evolution mechanism of coke species on the catalysts are identified. Furthermore, the review elaborates on how super-resolution imaging deepens the understanding of fundamental catalytic mechanisms at the nanoscale, providing theoretical support for the rational design of high-performance catalysts—such as pore structure optimization, acid site regulation, and coking suppression—and concludes with an outlook on current challenges and future directions.

Key words: super-resolution fluorescence imaging; zeolite catalysts; mass transfer diffusion; acid sites; coking



Industrial catalytic processes constitute the core of modern chemical industry, and their efficiency and selectivity directly determine energy utilization and conversion efficiency, environmental impact, and production costs^[1–4]. Zeolite catalysts have become indispensable materials in petroleum refining, chemical synthesis, and related fields due to their well-defined micropores and tunable acidity. The macroscopic performance of catalysts is essentially determined by their

microscopic structure, among which mass transfer efficiency, accessibility of acid sites, and coking behavior are three key microscopic factors constraining their activity and selectivity^[5–14].

Traditional characterization techniques (e.g. XRD, N₂ physisorption, and TPD, etc.) exhibit significant limitations in resolving the microstructural properties of the zeolite catalysts^[15–29]. These techniques mostly provide bulk-averaged information or static *ex situ* data, making it

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difficult to achieve *in situ* observation of dynamic processes such as mass transfer, acidity and coke formation under real reaction conditions involving high temperature, high pressure, and flowing media^[30–33]. This deficiency in understanding the microscopic mechanisms has long kept the correlation between catalyst structure and performance in a “black-box”. In the 400 kt/a polypropylene unit of PetroChina Lanzhou Petrochemical Company, the fluctuation in product selectivity caused by the non-uniform distribution of acid sites in the ZSM-5 catalyst exemplifies the manifestation of the aforementioned technical bottleneck in industrial practice^[34].

In recent years, the rise of super-resolution fluorescence imaging technology has provided a novel pathway to overcome the bottleneck. By ingenious designing molecular probes, such as merocyanine-based dyes with excellent photostability and environmental sensitivity, the technique utilizes fluorescence signal inversion to surpass the optical diffraction limit. The breakthrough enables the combination of nanoscale spatial resolution with exceptional *in situ* imaging capabilities. This enables to “visualize” the transport pathways of reactant molecules within the nanoscale channels of catalysts, accurately map the spatial distribution of acid sites and assess their accessibility, and even directly track the dynamic formation and evolution of coke species—all in environments approaching real reaction conditions. The team led by Weckhuysen has achieved a series of breaking in this field. For instance, the application of single-molecule fluorescence tracking technology enabled the first-ever measurement of local diffusion coefficient distributions within industrial catalyst particles. Furthermore, through super-resolution imaging, they successfully revealed nanoscale heterogeneity in the activity across the catalyst particles^[35]. In the methanol-to-olefins (MTO) reaction, *in situ* UV-vis and fluorescence microscopic imaging are employed to track the formation and evolution of coke species within individual H-ZSM-5 crystals in real time. The study suggested that polycyclic aromatic hydrocarbons preferentially form at the crystal edges and pore intersections, providing direct evidence for the catalyst deactivation^[36–37]. The results demonstrate that super-resolution fluorescence imaging technology not only addresses the longstanding “black-box” in industrial catalysis, but also provides a new visual, data-driven tool for catalyst screening, lifespan prediction, and structural optimization.

This paper will systematically elucidate the principles and characteristics of various super-resolution fluorescence imaging techniques, with a particular focus on discussing the latest applications in addressing key microscopic behavioral challenges in industrial zeolite catalysts, such as mass transfer, acidity, and coke deposition. By establishing precise correlations between nanoscale microstructure and macroscopic performance degradation, this review aims to elucidate the intrinsic mechanisms of catalyst deactivation and enhancement. It further seeks to develop microscopic design principles for catalysts with high coke resistance and

efficient diffusion, providing theoretical foundations and practical pathways for targeted development of a new generation of high-performance zeolite catalysts.

1 Fluorescence microscopy

1.1 Confocal laser scanning microscopy (CLSM)

Confocal fluorescence microscopy has emerged as a powerful tool for analyzing the multiscale structure of industrial catalysts, thanks to its unique optical sectioning capability^[38–46]. By employing a pinhole device, this technique effectively filters out fluorescence interference from out-of-focus planes. A typical optical path configuration of the system is illustrated in Figure 1. The point-scanning mechanism combined with pinhole-conjugate detection enables the acquisition of two-dimensional optical sections with high signal-to-noise ratio. In catalyst characterization, this advantage allows layer-by-layer analysis of fluorescence signals at varying depths within the particles. Consequently, it facilitates the three-dimensional reconstruction of catalyst spatial structures, providing direct evidence to elucidate critical aspects such as mass transfer and active site distribution in industrial catalysts.

To overcome the spatial resolution limitations imposed by the optical diffraction limit, multiple research teams have developed innovative super-resolution imaging strategies. Based on a confocal system, the research by Zhang has developed parallel detection pixel reassignment and fluorescence emission difference techniques. The technology utilizes spatial light modulators to precisely control the excitation light field and significantly enhances three-dimensional resolution while maintaining high-speed imaging capabilities through algorithmic optimization^[47]. The team of Zhao proposed a reflective differential confocal technique, which integrates bilateral fitting with super-resolution restoration algorithms, achieving nanometer-level axial resolution and high environmental stability^[48].

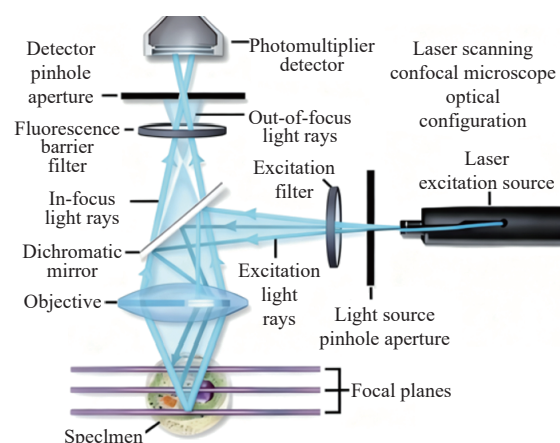


Fig. 1 Schematic diagram of a confocal fluorescence microscope

The multidimensional advancements in confocal technology now enable precise capture of three-dimensional structures and dynamic evolution within complex catalyst systems. By enabling *in situ* monitoring of critical parameters such as pore structures, active site distribution, and coking behavior, the technology provides a robust foundation for rational catalyst design and process optimization, effectively illuminating the opaque “black box” in traditional development approaches.

1.2 Total internal reflection fluorescence microscopy (TIRFM)

Total Internal Reflection Fluorescence Microscopy (TIRFM) demonstrates significant advantages in studying surface processes of industrial catalysts, leveraging its unique principle of evanescent wave excitation. The technique selectively excites samples using evanescent waves generated by total internal reflection, with a typical working principle illustrated in Figure 2. Since the penetration depth of evanescent waves perpendicular to the interface is strictly confined to nanometer scale (typically 100–200 nm), this technique can precisely restrict the excitation region to the catalyst surface and near-surface area which eliminates the interference from bulk fluorescence, resulting in exceptionally high signal-to-noise ratios and contrast during imaging^[49–53].

The unique surface-selective imaging capability makes TIRFM an ideal tool for investigating the physicochemical processes on catalyst surfaces. For instance, Frederice’s team successfully achieved *in situ* imaging of charge injection processes in CdS/TiO₂ composite materials by employing sequential fluorescence imaging in combination with resazurin and resorufin fluorescent probes. This approach clearly revealed the differences in charge injection efficiency between CdS/TiO₂ and SiO₂/TiO₂/CdS structures, directly correlating the differences with macroscopic hydrogen production performance. It thus provides a powerful means for understanding the “structure-performance” relationship at the single-particle scale and enables rational catalyst design^[54].

1.3 Super-resolution fluorescence microscopy (SRFM)

While both confocal and two-photon techniques enhance the resolution of optical microscopy, they remain constrained by the diffraction limit. To overcome the problem, various super-resolution fluorescence microscopy techniques have been developed. Examples include structured illumination microscopy (SIM), stimulated emission depletion microscopy (STED), and single-molecule localization-based techniques such as stochastic optical reconstruction microscopy (STORM) using organic dyes, as well as photoactivated localization microscopy (PALM/fPALM) employing fluorescent proteins. Stochastic Optical Reconstruction Microscopy (STORM) achieves super-resolution imaging by temporally separating the emission behaviors of fluorescent molecules. As illustrated in Figure 3, the process begins by using photoswitchable fluorescent probes to randomly activate a sparse subset of molecules into an emissive state under controlled activation laser illumination, ensuring that the spacing between adjacent molecules exceeds the diffraction limit. Subsequently, the activated molecules are excited to emit fluorescence whose diffraction-limited spots are captured by a highly sensitive camera. Using single-molecule localization algorithms, the central position of each fluorescence spot is determined with nanometer-level precision (typically within 20–30 nm). Through tens of thousands of cycles of “activation-localization-quenching”, precise positional information for all fluorescent molecules within the sample is collected. Ultimately, all localized coordinates are reconstructed into a comprehensive super-resolution image. The approach breaks through the optical diffraction limit, enabling nanoscale visualization of critical processes within catalysts such as internal pore structures, active site distribution, and the evolution of reaction intermediates. It thereby provides direct observational evidence for mechanistic analysis and performance optimization of industrial catalysts^[55–58]. For example, Weckhuysen’s team employed single-molecule super-resolution imaging for the first time to quantitatively reveal the difference of up to an order of magnitude in catalytic activity among distinct zeolite domains within industrial FCC catalyst particles^[59].

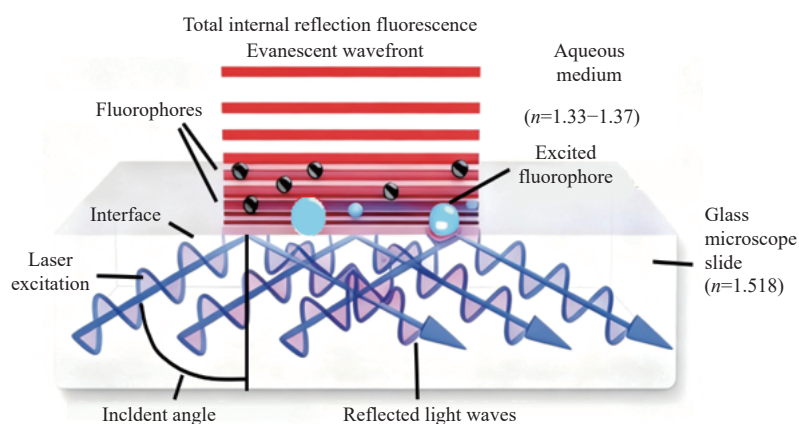


Fig. 2 Schematic diagram of total internal reflection fluorescence microscopy (TIRFM)

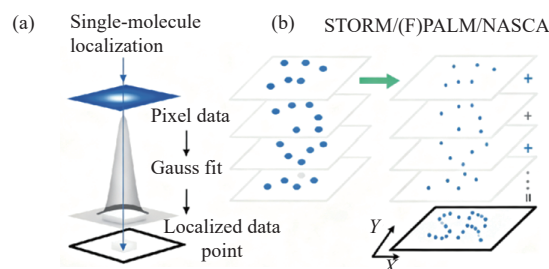


Fig. 3 Schematic diagram of stochastic optical reconstruction microscopy (STORM)

1.4 Other related fluorescence techniques

Beyond the mainstream fluorescence microscopy techniques discussed above, fluorescence lifetime imaging (FLIM) and single-molecule fluorescence imaging also offer unique perspectives for catalyst characterization^[60–65]. FLIM detects the excited-state lifetime of fluorophores to sensitively probe microenvironmental characteristics (such as polarity and pH value) on the catalyst surfaces, thereby realizing the analysis of localized chemical interactions. Single-molecule imaging, by analyzing individual fluorescence signals, directly reveals the heterogeneity in activity distribution within and across the catalyst particles, overcoming the averaging limitations inherent in bulk measurements. For instance, the team led by Zürner et al.^[66] employed single-molecule tracking to visualize the diffusion trajectories of individual molecules within mesoporous materials for the first time, directly elucidating the pore transport characteristics from the perspective of mass transfer. Hendriks et al.^[67] further correlated the single-molecule signals with the accessibility of acid sites and the mechanisms of coking-induced deactivation within the catalyst particles, thereby bridging the gap from physical observation to chemical processes.

2 Selection principles and mechanism of action of fluorescent probes

Fluorescent probes serve as the core element of super-resolution fluorescence imaging techniques whose appropriate selection and design directly determine the accuracy and reliability of experimental outcomes. In zeolite catalyst research, fluorescent probes must be selected according to the objectives such as mass transfer, acid sites, and coke formation.

For mass transfer studies, physical tracers such as rhodamine B and merocyanine are typically employed. The probes diffuse along concentration gradients, enabling clear visualization of molecular transport pathways within pore networks through time-series imaging. In the characterization of acid sites, the selection of fluorescent probes primarily encompasses three categories: basic recognition probes, reactive conversion probes, and polymer-tagged probes. Representative alkaline organic molecules such as DAMPI and Nile Blue A contain

nitrogen-rich molecular structures that specifically interact with Brønsted acid sites. This binding induces significant changes in fluorescence quantum yield or emission wavelength, enabling nanoscale spatial localization and semi-quantitative analysis of acid strength. Reactive probes such as thiophene and furfuryl alcohol undergo acid-catalyzed oligomerization to form highly fluorescent oligomers. The location and intensity of the resulting fluorescence signals directly reflect the spatial distribution of the acid sites and their activity. *p*-methylstyrene, functioning as a polymer-tagged probe, undergoes cationic polymerization initiated by acid sites to form fluorescent polymer chains. This characteristic makes it an effective tool for investigating acid site accessibility and activity. The three types of probes each offer distinct advantages, providing multi-dimensional solutions for characterizing zeolite acidity through static recognition, dynamic reaction, and polymerization labeling, respectively. For coking behavior monitoring, two complementary strategies are primarily adopted: firstly, label-free imaging based on the intrinsic fluorescence of carbon deposits, which effectively distinguishes the carbon species with varying degrees of graphitization by analyzing spectral characteristics. Secondly, the use of reactive probes such as thiophene and furfuryl alcohol, which generate highly fluorescent products through catalytic reactions on acid sites, thereby indicating active sites prone to coking and potential reaction pathways.

In summary, the selection of fluorescent probes for imaging studies of zeolite catalysts must adhere to specific mechanisms tailored to different research scenarios. The investigation of mass transfer processes primarily relies on the principle of physical diffusion tracing. The acidity characterization depends on specific interactions between probes and acid sites. While coking monitoring can be achieved through two complementary approaches: direct detection *via* intrinsic fluorescence and reaction pathway tracing. A thorough understanding of the mechanistic differences and the appropriate selection of probes hold theoretical guidance and practical value for establishing accurate “structure-performance” correlations in catalysts.

3 Fluorescence imaging unveils mass transfer resistance and diffusion pathways

3.1 Correlation between catalyst structure and mass transfer performance

Kumar et al.^[68] developed a confocal fluorescence microscopy method based on fluorescent staining, enabling chemical imaging of individual zeolite domains within the FCC catalyst particles at nanoscale while simultaneously staining the matrix material. Reis et al.^[69] synthesized two reactive phenanthrene derivatives with high quantum yields as fluorescent markers for the microscopic imaging of surface-modified micron-sized zeolite L. The approach offers a novel method for the visualization of zeolite-based

catalysts. Li et al.^[70] employed single-particle fluorescence spectroscopy to image charge carrier transport in facet-dependent semiconductor photocatalysts, thereby revealing the distribution of active sites and charge transfer pathways. In summary, fluorescence microscopy imaging, with the powerful capability for spatiotemporally resolved visualization of mass transfer, has become a key approach for establishing correlations between catalyst structure and performance, opening new directions for mass transfer research.

Building upon the technical foundation, our team employed laser scanning confocal microscopy and single-molecule super-resolution fluorescence imaging to address the mass transfer limitations of traditional kaolin-based catalysts (CAT-1) i.e. five FCC catalysts with different matrix materials were synthesized. Using Rhodamine B staining (Figure 4(a))^[71] and fluorescence imaging analysis, the mass transfer of catalysts doped with various matrix materials was evaluated. The results indicated that the catalyst using the independently developed macroporous Brønsted acid-rich matrix APM-9 (CAT-6) exhibited significantly optimized mesoporous structure, with a mass transfer diffusion coefficient up to 25 times that of conventional catalysts, achieving a breakthrough in performance.

Furthermore, the imaging technique was employed to investigate the mechanism by which crystallization time affects the mass transfer performance of the catalysts. By controlling the *in situ* crystallization time (1, 8, 16 and 24 h), four types of FCC catalysts with varying Y-zeolite content were prepared. Combining breakthrough experiments with acridine probe staining (Figure 4(b))^[72], fluorescence imaging results confirmed that the distribution of Y-zeolite could be precisely controlled *via in situ* crystallization, thereby optimizing the pore structures—a key strategy for achieving superior mass transfer performance.

3.2 Mass transfer bottlenecks in crystal structures and hierarchical pore optimization

Zeolite crystals are typically composed of multiple intergrown subcrystalline domains with varying orientations. The complexity of the internal pore structures leads to significant anisotropy in reactant diffusion. Karwacki et al.^[73] utilized fluorescence imaging to reveal that the 90° intergrowth structure within ZSM-5 crystals results in alternating straight and sinusoidal channels, forming a “diffusion maze”. Ristanović et al.^[59] further employed single-molecule imaging to unveil significant differences in diffusion rates and activities among distinct subcrystalline domains, confirming the profound impact of intracrystalline diffusion heterogeneity on the catalytic processes.

To overcome the diffusion limitations caused by the inherent crystal structure, constructing a hierarchical pore system has proven to be an effective strategy. Zhu et al.^[74] introduced fluorine ions during the synthesis of SSZ-13 zeolite (SSZ-13-10F), creating a hierarchical structure rich in secondary micropores (0.46–0.7 nm). Fluorescence imaging results demonstrated that the reaction signals achieved full penetration throughout the modified crystals (Figure 5), significantly enhancing the diffusion efficiency of the reactants and the products. Consequently, the material exhibited prolonged catalyst lifespan and higher carbon tolerance in the MTO reaction.

In methodological terms, Hendriks et al.^[75] utilized confocal fluorescence microscopy combined with a series of increasingly sized DAMPI-based fluorescent probe molecules. Through three-dimensional imaging and polarization-dependent measurements, they systematically revealed the adsorption behavior and alignment orientation of the probe molecules within pores of different sizes (Figure 6(a)), offering a novel approach for assessing zeolite accessibility.

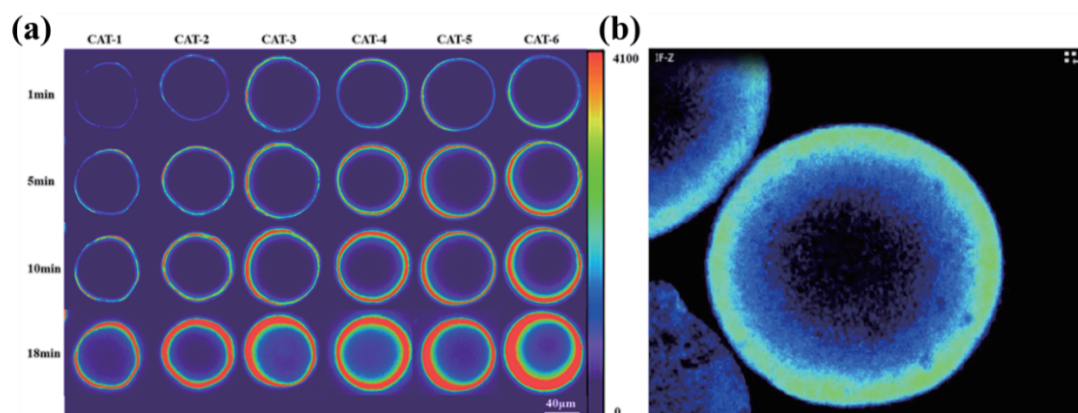


Fig. 4 (a) Time-series fluorescence images of Rhodamine B diffusion in catalyst microspheres (CAT-1 to CAT-6)^[71]; (b) Laser scanning confocal fluorescence mapping of zeolite Y distribution in CAT-24 microspheres^[72] (with permission from CIESC Journal and Elsevier)

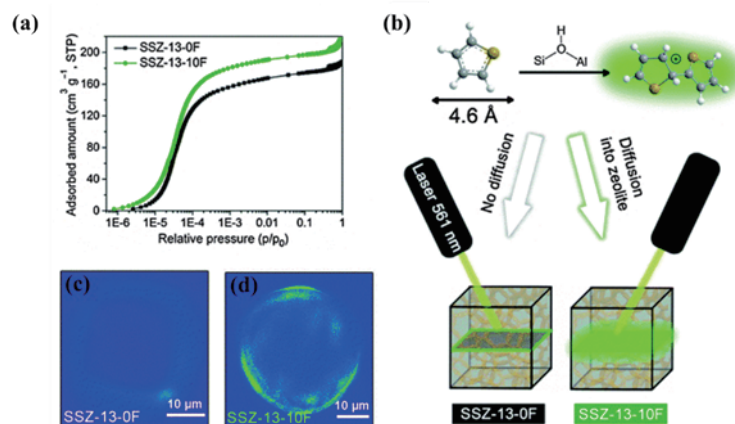


Fig. 5 Hierarchical pore structure and diffusion performance of SSZ-13-0F (parent) and SSZ-13-10F (F-modified): (a) Ar physisorption isotherms; (b) Thiophene oligomerization reaction mechanism; (c), (d) Fluorescence micrographs of SSZ-13 single crystals after reaction (120 °C, detection range 570–620 nm)^[74] (with permission from RSC Publications)

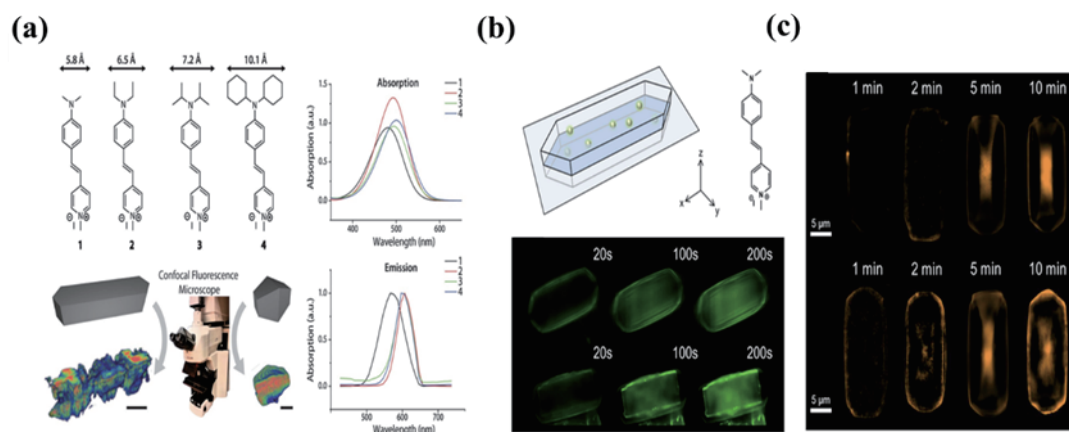


Fig. 6 (a) Molecular probe characterization and zeolite diffusion study^[75]; (b) Super-resolution fluorescence microscopy study of ZSM-5 single crystal diffusion behavior^[76]; (c) Spatiotemporal fluorescence behavior comparison of ZSM-5-P and ZSM-5-H in catalytic furfuryl alcohol condensation^[77] (with permission from Wiley-VCH and Elsevier)

The team led by Peng et al.^[76–77] further employed structured illumination microscopy (SIM) in conjunction with non-reactive and reactive probes to achieve dynamic visualization of diffusion processes inside the ZSM-5 zeolite. The results suggested that acid etching effectively reduces the surface diffusion barriers, facilitating the mass transfer of reactants into the crystal interior and thereby significantly enhancing the catalytic reaction rates (Figure 6 (b), (c)).

3.3 Catalytic mass transfer mechanisms and industrial optimization pathways

In industrial processes, optimizing the diffusion pathways of the catalysts is a critical step for enhancing the reaction efficiency. Fluorescence microscopy imaging not only accurately identifies the locations and extent of mass transfer limitations but also provides direct visual evidence

for the precise tuning of internal catalyst structures and the optimization of diffusion pathways. At the fundamental research level, multiple studies have demonstrated the value of the technology in elucidating the mechanisms linking mass transfer and reaction processes. Hendriks et al.^[78] utilized single-molecule fluorescence tracking to analyze the diffusion trajectories of PDI probe molecules within FCC catalyst particles, providing a direction for establishing correlations between “structure-mass transfer-reaction performance” at the single catalyst particle level or within other hierarchical materials. Park et al.^[79] employed total internal reflection fluorescence microscopy to observe the fluorescence trajectories of individual molecules in a Diels-Alder reaction with high temporal resolution (~100 ms). By analyzing the intensity variations, they identified the reaction intermediates and successfully quantified the kinetic parameters for state transitions, thereby revealing the microscopic kinetics of organocatalytic reactions at the single-molecule level. Reis et al.^[80] applied the technique to

the palladium-catalyzed Suzuki-Miyaura cross-coupling reaction, analyzing the fluorescence blinking trajectories to calculate the single-molecule turnover frequencies. This approach provides a novel method for assessing the impact of catalyst loading on catalytic efficiency.

In the realm of industrial catalyst design, our team employed super-resolution fluorescence microscopy and single-molecule trajectory tracking to systematically reveal the identification and modulation mechanisms of surface mass transfer barriers in ZSM-5 zeolite (Figure 7)^[81]. The study suggested that due to the micropore limitations in conventional ZSM-5 (CAT-0), probe molecules could only diffuse to the crystal edges, resulting in significant mass transfer barriers. In contrast, the CAT-W sample, prepared *via* template-protected alkaline treatment, successfully constructed a continuous mesoporous system while maintaining the integrity of the crystal structure. This led to an approximately 1.39-fold increase in the effective diffusion coefficient of probe molecules, significantly enhancing the mass transfer efficiency within the support and enabling high-efficiency transport from the surface to the interior. This research clarifies the structure-activity relationship of “template protection-mesopore construction-diffusion enhancement” at the microscale, offering critical guidance for the rational design of industrial catalysts.

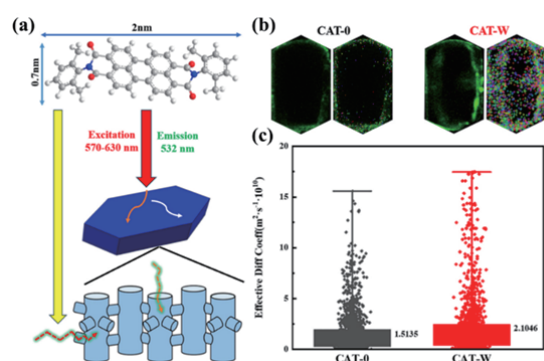


Fig. 7 Characterization of molecular trajectories and diffusion properties within the catalyst particles: (a) Schematic diagram of PDI probe molecule trajectories in ZSM-5 pore channels based on confocal fluorescence microscopy; (b) Schematic diagram of single-molecule localization and trajectory tracking of fluorescent molecules on zeolite surfaces; (c) Distribution of actual effective diffusion coefficients (D_e') for three zeolite samples^[81] (with permission from Elsevier)

4 Analysis of acid sites accessibility

4.1 Multiscale characterization of spatial distribution and accessibility of acid sites

As the key active centers in industrial catalysts, the spatial distribution and accessibility of acid sites directly determine the efficiency of the catalytic reactions. However,

traditional characterization methods can only reflect average acidity information of the catalysts, making it difficult to reveal the microscale heterogeneous characteristics. In recent years, the emergence of fluorescence microscopy techniques has provided powerful tools for *in situ*, high-resolution imaging of acid sites.

In studying the deactivation mechanisms of industrial fluid catalytic cracking (FCC) catalysts, Buurmans et al.^[82] innovatively developed a dual-probe confocal fluorescence staining strategy using thiophene and Nile Blue A. The technique successfully enabled simultaneous visualization and quantitative analysis of zeolite active centers and Brønsted acid sites at the single-particle level. It not only clearly revealed significant acidity heterogeneity within and between particles but also, more importantly, established a positive correlation between fluorescence intensity and the activity (Figure 8). This confirmed a quantitative “acidity-activity” relationship in an industrial catalyst for the first time, providing direct evidence for understanding the dynamic evolution of acid sites during the catalyst deactivation.

Furthermore, in their study on acid sites imaging of H-ZSM-5 zeolite crystals, quantitative three-dimensional single-molecule fluorescence microscopy was employed to precisely measure the catalytic activity of different acid sites^[83]. The results showed that mild steam treatment at 500 °C significantly enhanced the acid site accessibility by introducing mesoporous structures, increasing the local catalytic turnover frequency by up to fourfold. In contrast, steam treatment at 700 °C led to substantial dealumination, significantly reducing both the number of acid sites and the turnover frequency, clearly demonstrating the critical regulatory role of pore structure on acidic reactivity.

By integrating dark-field microscopy imaging with temperature-programmed desorption (TPD), the team led by Yi et al.^[84] developed the optical temperature-programmed desorption (oTPD) method. By real-time tracking of the scattering intensity changes of individual zeolite nanoparticles during ammonia desorption, this method enables intrinsic evaluation of the quantity, strength, and desorption kinetics of acid sites. The technique not only reveals heterogeneity in acid properties at the single-particle level but also establishes, for the first time, a linear relationship between acid strength and silicon island content, offering a new perspective for understanding structure-acidity relationships.

Building upon traditional imaging methods, our team integrated super-resolution fluorescence microscopy with GIS-based spatial quantitative analysis. Through nearest-neighbor distance analysis, precise characterization of the spatial distribution of acid sites within ZSM-5 zeolite was achieved^[85]. As shown in Figure 9, by statistically analyzing the spatial distances between active acid sites, it was confirmed that after alkaline treatment, the number of acid sites in regions larger than 10 nm increased significantly. This finding indicated that alkaline treatment effectively eliminated the surface diffusion barriers, allowing originally

embedded acid centers to be fully exposed, thereby addressing the distribution challenge of acid sites being “accessible yet not densely clustered.”

In collaboration with the PetroChina Lanzhou Petrochemical Research Center, we employed spatiotemporally resolved fluorescence imaging to systematically elucidate the inherent trade-off mechanism between particle size and acid site accessibility in FCC catalysts^[86]. The results

suggested that small-particle catalysts (CAT-1: 10–20 μm), benefiting from abundant submicron pores ($< 0.2 \mu\text{m}$) and shorter diffusion pathways, achieved full penetration of acid sites within 3 min. In contrast, large-particle catalysts (CAT-6: 120–180 μm) suffered from significantly extended mass transfer pathways, resulting in severely reduced accessibility in the core regions (Figure 10).

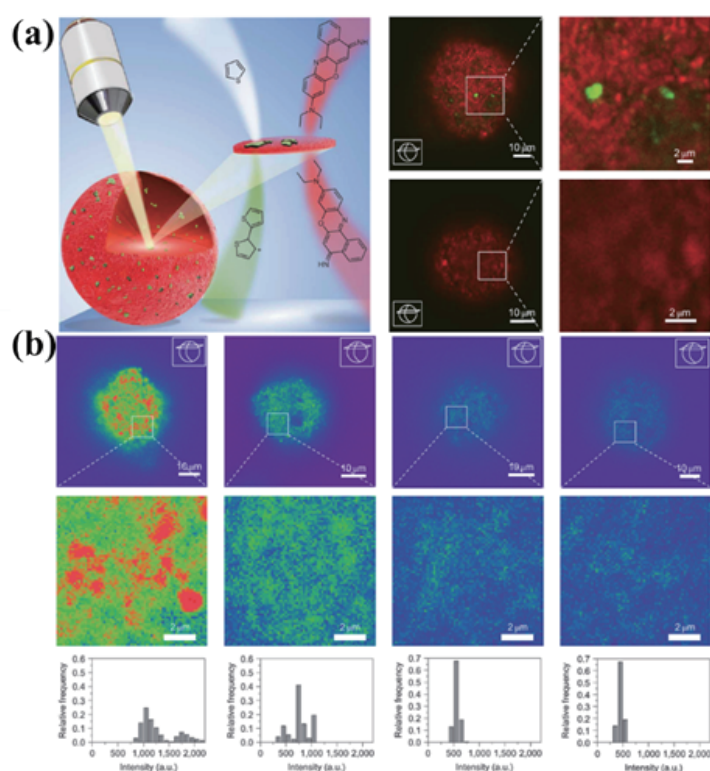


Fig. 8 (a) Confocal fluorescence micrographs of dual-stained FCC catalyst particles; (b) Fluorescence characterization and intensity distribution of FCC-1 catalyst at different deactivation stages^[82] (with permission from Springer Nature)

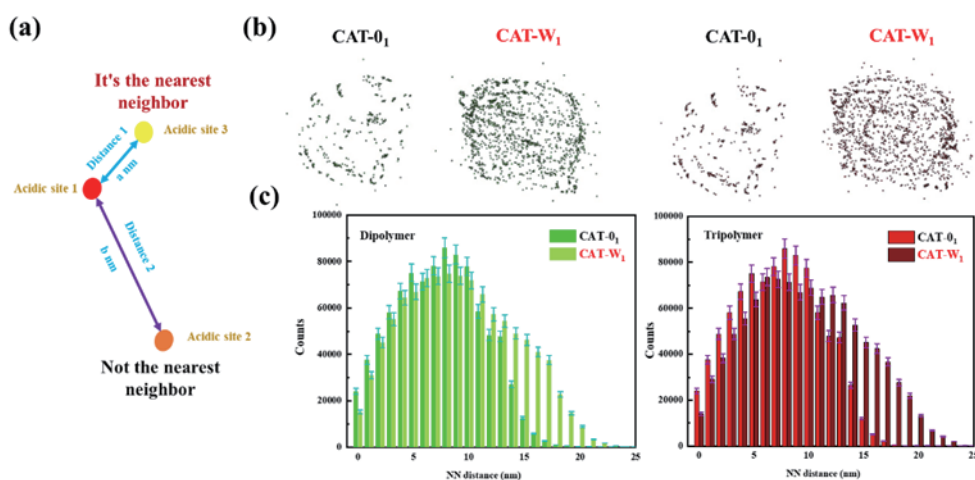


Fig. 9 (a) Schematic diagram of nearest neighbor distance analysis; (b) The distribution map; (c) Histogram of the nearest neighbor distance of active sites in molecular sieve samples^[85] (with permission from Elsevier)

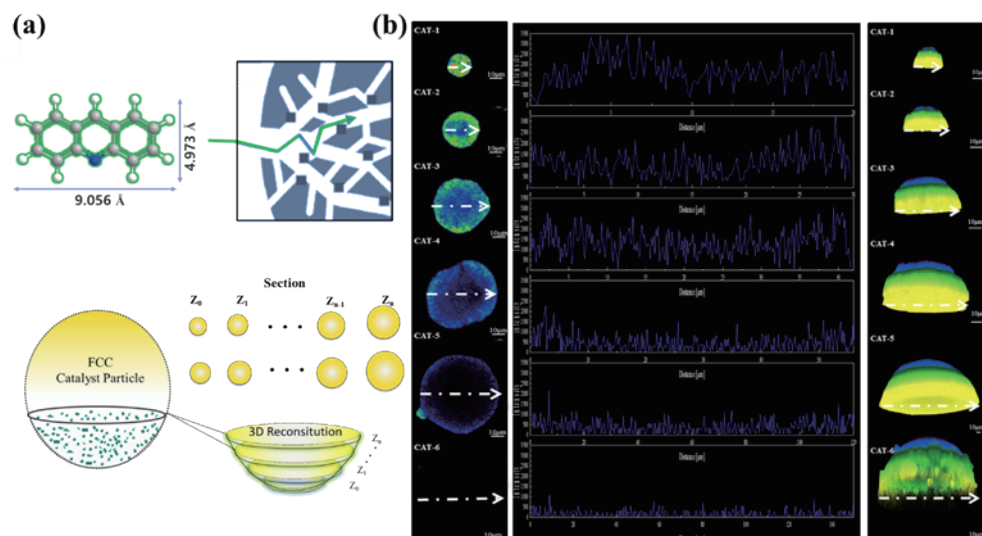


Fig. 10 (a) Schematic diagram of acridine probe diffusion pathways within FCC catalyst particles; (b) Maximum cross-sectional fluorescence intensity and 3D reconstruction models of FCC particles with different sizes^[86] (with permission from Springer Nature)

Based on the studies at the single-particle level, a quantitative structure-activity relationship among “particle size, pore structure, and mass transfer efficiency” were established. Accordingly, we propose that precisely controlling the catalyst particle size within the range of 10–50 μm is a key strategy to overcome the mass transfer resistance and optimize the reaction efficiency.

4.2 Spatial heterogeneity and regulatory mechanisms of acid site utilization efficiency

In the study of reaction heterogeneity within industrial FCC catalyst particles, Ristanović et al.^[59] employed single-molecule fluorescence super-resolution imaging techniques (NASCA and SOFI) to realize quantitative imaging of catalytic activity in submicron ZSM-5 aggregates inside the catalyst particles for the first time. The study revealed significant differences in Brønsted acidity and turnover frequencies among distinct zeolite domains within the same particle, with utilization efficiency of active sites varying by up to an order of magnitude. This work unveils the substantial heterogeneity in active site utilization efficiency within the catalysts at the nanoscale, providing direct evidence for optimizing the performance of industrial catalysts.

The team further employed single-molecule fluorescence microscopy to track, in real time, the formation of fluorescent oligomers from styrene derivatives on Brønsted acid sites of zeolites which established a novel method using individual fluorescence events as counts for catalytic conversions. Local turnover frequencies at the nanoscale were calculated, enabling precise evaluation of the utilization efficiency of active sites in different regions of the crystal^[87]. The study also found that photostable trimers preferentially form in defect-rich regions, providing a new nanoscale spectroscopic marker for assessing the zeolite quality.

Leveraging methodological innovation, the team used

furfuryl alcohol as a probe. By precisely counting fluorescence events and calculating the local turnover frequencies, they quantified, for the first time in three-dimensional space, the impact of steam treatment on the utilization efficiency of active sites across different regions of H-ZSM-5 (Figure 11)^[88]. The study revealed that after mild steam treatment, the turnover frequency in the near-surface regions of the crystals could be up to four times higher than in the bulk, though the distribution of utilization efficiency was highly uneven. In contrast, severe steam treatment caused the overall turnover frequency to plummet by 460-fold. Combined with TOF-SIMS elemental analysis, the intrinsic correlation between aluminum migration and active site utilization efficiency was clarified.

By employed ZSM-5 as a model system, our team constructed a hierarchical pore system (2–5 nm) using template-protected alkaline etching (Figure 12)^[85]. Thiophene was selected as probe molecule for the catalytic conversion to fluorescent trimers on Brønsted acid sites to compare the actual accessibility of acid sites in hierarchical pore versus microporous zeolites. The results showed a 114% increase in fluorescence signal density of trimeric products in the former, experimentally confirming the significant enhancement of active site utilization efficiency by the hierarchical pore structure.

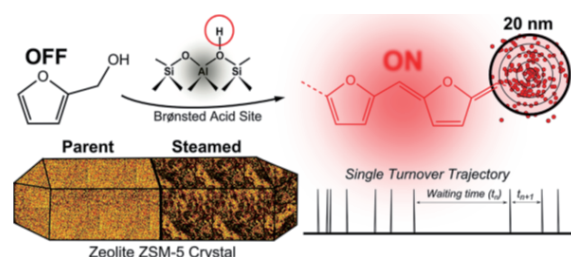


Fig. 11 Conversion frequency of furfuryl alcohol probe on ZSM-5 zeolite^[88]

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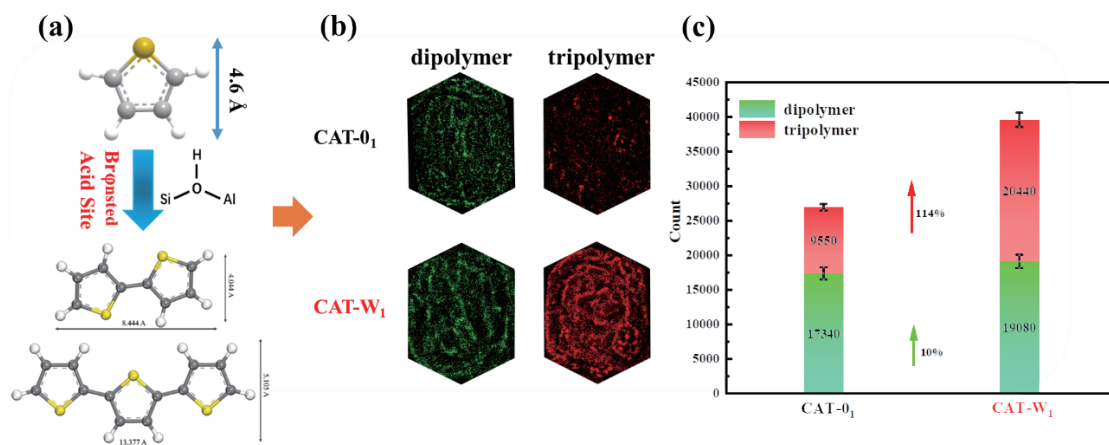


Fig. 12 (a) Schematic diagram of thiophene reaction pathway; (b) Single-molecule imaging of acid site distribution for thiophene dimerization (green) and trimerization (red) products on ZSM-5 surface; (c) Statistical comparison of acid site quantities corresponding to dimerization and trimerization products^[85] (with permission from Elsevier)

5 Investigation of catalyst coking behavior

5.1 Localization and Identification of coke species

Coke deposition is one of the key factors leading to catalyst deactivation. Traditional characterization methods struggle to enable *in situ* observation of the spatiotemporal evolution of coke species at the nanoscale. However, the fluorescence imaging technology offers a breakthrough tool for this purpose.

In the study of catalytic pyrolysis of polypropylene to produce aromatic hydrocarbons (BTX), Weckhuysen's team combined *in situ* fluorescence microscopy, UV-vis spectroscopy, and solid-state NMR to achieve, for the first time, *in situ* visualization of aromatic intermediate evolution at the nanoscale during the reaction^[89]. As shown in Figure 13,

it was found that the spent industrial FCC catalysts (ECAT), due to their moderate acidity and excellent structural accessibility, could significantly suppress graphitic carbon deposition while maintaining 20% of aromatic yield. This phenomenon revealed the synergistic mechanism between zeolite and matrix domains in coke formation.

In the methanol-to-olefins (MTO) reaction, the coke-induced deactivation in ZSM-5 zeolite has long constrained its industrial application. Mores et al.^[90] further combined *in situ* UV-vis microspectroscopy with confocal fluorescence microscopy to unveil the microscopic pathways of coke evolution: during the initial reaction stage, methyl-substituted aromatic carbocations formed, gradually developing into linear polycyclic aromatic hydrocarbons, and ultimately leading to the formation of non-removable graphitic carbon on the catalyst surface.

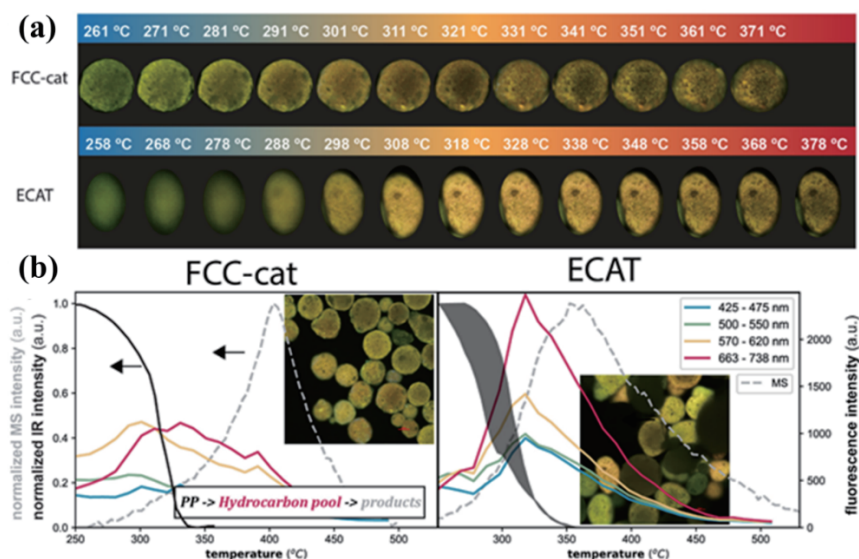


Fig. 13 Coke and product evolution during polypropylene pyrolysis over FCC-cat and ECAT: (a) Temperature-dependent fluorescence micrographs of coke spatial distribution (260–380 °C); (b) Fluorescence spectra of coke species^[89] (with permission from RSC Publications)

Polarization spectroscopy further confirmed that large coke molecules preferentially align along the straight channels of ZSM-5 (Figure 14)^[90]. Moreover, acid density played a critical regulatory role in coking behavior i.e. high acid density significantly accelerated coke formation. However, when the Si/Al ratio exceeded 17, reaction temperature, instead of the acid density, became the dominant factor.

To further reveal the spatial distribution patterns of coke deposition, the teams of Zenobi and Kumar, in collaboration with Weckhuysen's team, combined hyperspectral confocal fluorescence microscopy with tip-enhanced fluorescence microscopy. For the first time, they mapped a “spatiotemporal atlas” of coke evolution on ZSM-5 catalysts at the nanoscale (Figure 15)^[91]. The results revealed that during the initial reaction stage, small methylated aromatic molecules predominantly accumulated in the crystal center, while graphite-like carbon preferentially formed at the crystal edges. As the reaction progressed, graphitic coke gradually spread across the entire crystal surface, ultimately leading to catalyst deactivation. Even more remarkably, the TEFL technique, with its approximately 35 nm ultra-high resolution, visually demonstrated that step edges on the

crystal surface exhibited higher catalytic activity and a greater tendency for coke deposition, suggesting the inherent heterogeneity in the distribution of active sites on the catalyst surface.

5.2 Coking mechanisms and catalyst design optimization

To effectively suppress the catalyst coking and extend its service life, researchers have utilized advanced characterization techniques to elucidate the coking mechanisms and guide the design of catalyst structures. Significant progress has been achieved in several key catalytic systems.

In the methanol-to-olefins (MTO) reaction, by combining confocal fluorescence microscopy with hyperpolarized ¹²⁹Xe NMR spectroscopy, Gao et al.^[92] found that the coke deposition in SAPO-34 zeolite exhibited a “shell-rich” distribution pattern (Figure 16). This finding informed the optimization of diffusion pathways: by modulating crystal size and pore structure, diffusion limitations of reactants were effectively alleviated, significantly delaying the catalyst deactivation caused by coke deposition.

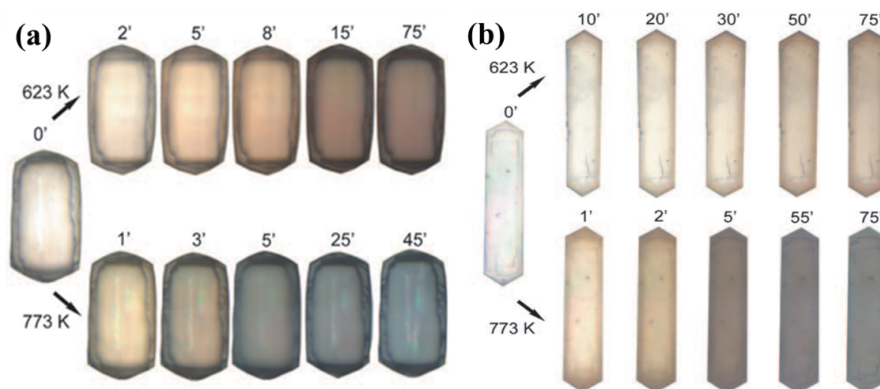


Fig. 14 Coke evolution in H-ZSM-5 zeolites with different Si/Al ratios at 623 and 773 K: (a) Si/Al=11; (b) Si/Al=17^[90] (with permission from Wiley-VCH)

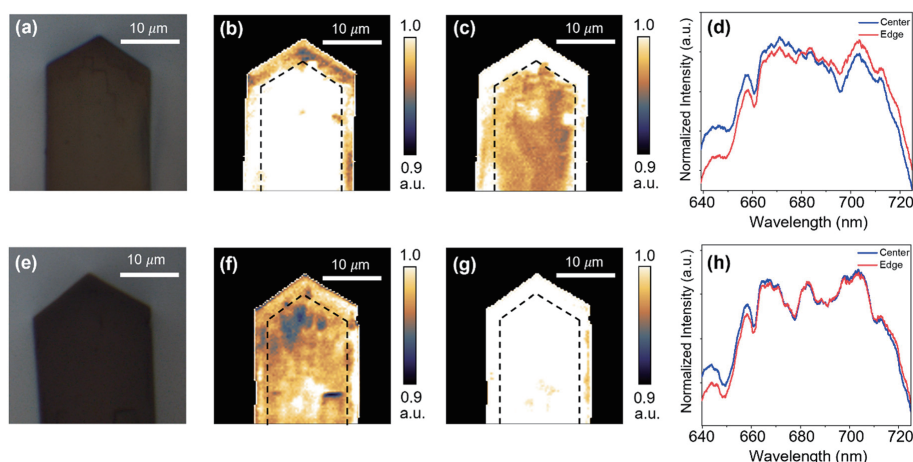


Fig. 15 Fluorescence images in the 640–730 nm range and fluorescence spectral distributions at the edge and center of ZSM-5 crystals at different reaction times: (a)–(d) 10 min; (e)–(h) 90 min^[91] (with permission from RSC Publications)

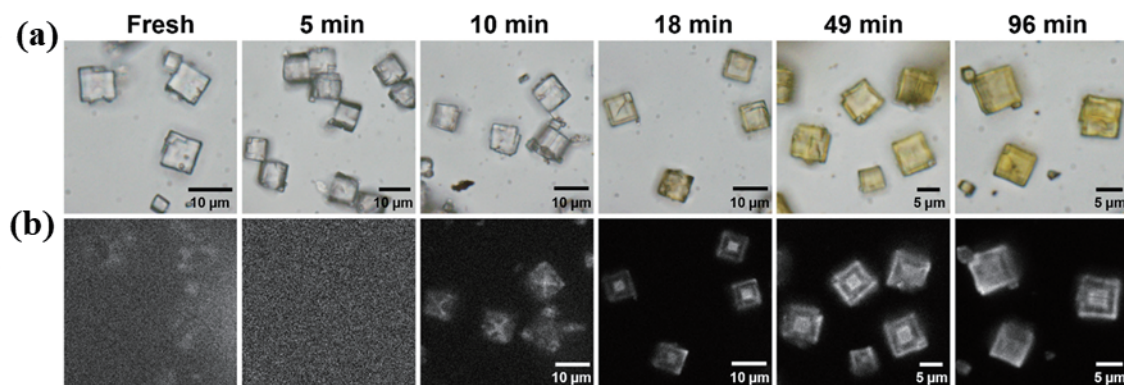


Fig. 16 Morphological and fluorescence characterization of SAPO-34 crystals after MTO reaction at 673 K with different reaction times: (a) Bright-field images; (b) Confocal fluorescence microscopy images^[92]
(with permission from Elsevier)

In the skeletal isomerization of oleic acid, the study further elucidated the regulatory role of pore structure on coking behavior. Based on polarized fluorescence analysis of Ferrierite single crystals (Figure 17)^[93], the entrance region of the 10-membered ring straight channels was identified as the preferential site for coke formation. This understanding provided clear direction for catalyst optimization: by modulating crystal size to increase pore entrance density, pore clogging could be effectively delayed, thereby significantly enhancing the catalyst

stability and service life during long-term operation.

To address the coking issue of Ni-based catalysts in the dry reforming of methane, the team led by Zu collaborated with our group to design a b-axis-oriented Ni@S-1 nanosheet catalyst (Figure 18)^[94]. By precisely controlling the nanosheet thickness to 60 nm, a dynamic balance between Ni⁰ and NiO_x(OH)_y active sites was achieved, establishing a self-regulated “coking-decoking” cycle. This enabled stable operation of the catalyst for 100 h at 750 °C, demonstrating the outstanding anti-coking performance.

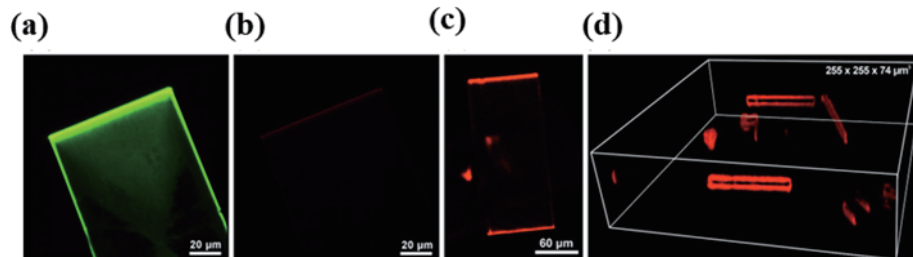


Fig. 17 Visualization of the pore-mouth catalysis mechanism *via* fluorescence imaging: (a), (b) Differential coking behavior at the entrances of 10-MR vs. 8-MR channels; (c), (d) Preferential occupation of the 10-MR channel entrances by coke species at (c) 2D and (d) 3D scales^[93]
(with permission from Wiley-VCH)



Fig. 18 Fluorescence spectra of coke formation over Ni@S-1-60 nm catalyst during methane dry reforming^[94]
(with permission from Elsevier)

Weckhuysen’s team combined atom probe tomography (APT) with confocal fluorescence microscopy (CFM) to

reveal, for the first time across scales (micro- to nano-), the intrinsic relationship between coke distribution and

nanostructure in Beta zeolites (Figure 19)^[95], elucidating the microscopic origins of non-uniform deactivation in industrial catalysts. Furthermore, by employing *in situ* UV-vis spectroscopy and confocal fluorescence microscopy, the team revealed, at the single-particle level, that coke precursors preferentially grew along the straight channels during template decomposition in ZSM-5 zeolite, eventually

distributing uniformly within the crystal. This discovery not only provided a theoretical basis for optimizing industrial calcination processes to avoid pore blockage but also opened new approach for designing shape-selective zeolite materials, regulating reaction pathways, and suppressing coke formation.

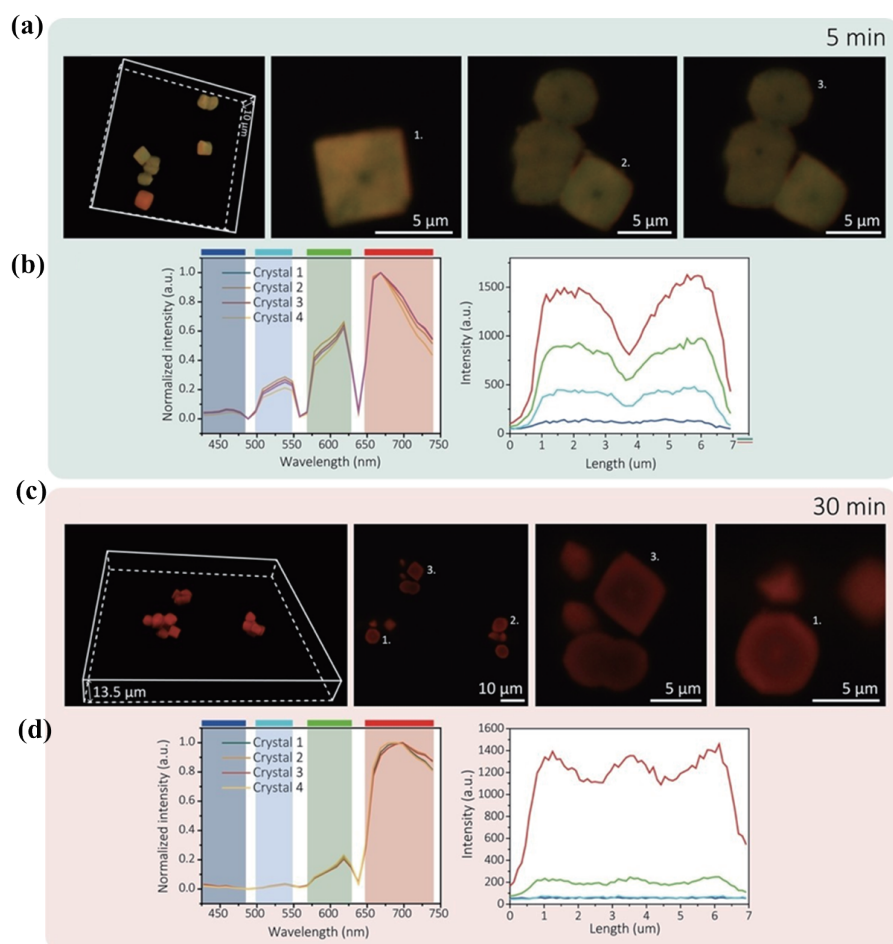


Fig. 19 Three-dimensional confocal fluorescence microscopy reconstruction and spectral analysis of Beta zeolites with different coke deposition times: (a), (b) 5 min; (c), (d) 30 min^[95]
(with permission from Wiley-VCH)

6 Conclusion and outlook

This article systematically reviews the latest advances in super-resolution fluorescence imaging technology for unraveling the “black box” in industrial zeolite catalysts. By enabling *in situ*, quantitative analysis of key microscopic processes such as mass transfer, acidity, and coke formation at the nanometer and single-molecule scales, the technology has successfully transformed industrial catalysts from “black boxes” into “transparent reactors.” The research reveals that mass transfer exhibit significant spatial heterogeneity within hierarchical pores. The accessibility of acid sites and their utilization efficiency show substantial nanoscale variations and coking behavior following distinct spatiotemporal evolution patterns. The insights gained from

the microscopic mechanistic studies provide theoretical foundations and clear optimization pathways for the precise design of industrial catalysts: For mass transfer optimization, constructing hierarchical pore systems and surface modifications can reduce the diffusion barriers. For acidity regulation, a synergistic approach is needed that precisely controls aluminum distribution and applies moderate steam treatment to balance the acid density, accessibility, and stability. In terms of anti-coking design, strategies such as shape-selective pore mouth passivation and crystal morphology control can effectively suppress the formation and deposition of the coke precursors.

Although fluorescence nanoscopy shows immense potential, its further advancement still faces several key challenges. Firstly, the technology heavily relies on the

development of high-performance fluorescent probes, yet the probe molecules themselves may intrude and interfere with the actual reaction microenvironment. Secondly, despite being termed “super-resolution,” the spatial resolution (typically 20–50 nm) remains far below that of electron microscopy, limiting the direct atomic-level structural analysis. Thirdly, the technique has limitations in imaging depth and sample compatibility, performing poorly with opaque, thick, or highly scattering samples. Moreover, designing *in situ* reaction cells suitable for real industrial conditions such as high temperature and high pressure remains a significant challenge. Lastly, prolonged laser exposure can cause photobleaching and phototoxicity, leading to fluorescence signal decay and potential damage to the catalyst surface, thereby compromising the authenticity of observations.

Looking ahead, the technology will continue to evolve along the four key directions: firstly, multimodal integration (e.g. fluorescence-IR, fluorescence-Raman) will enable simultaneous analysis of catalyst structure, composition, and reaction activity. Secondly, the deep integration of high-speed dynamic imaging with machine learning algorithms will facilitate precise capture and performance prediction of dynamic catalytic processes. Thirdly, research systems will expand from traditional zeolites to emerging materials such as metal-zeolite bifunctional catalysts and MOFs. Finally, advancements in *in situ* characterization will drive the transition of research environments from idealized conditions to real operating scenarios. Through continuous technological innovation and mechanistic exploration, fluorescence nanoscopy is poised to play an increasingly pivotal role in the “on-demand design” of future high-performance industrial catalysts. It will complement and synergize with theoretical simulations and artificial intelligence, collectively advancing heterogeneous catalysis science from fundamental understanding to industrial application.

Declaration of Competing Interest

The authors declare no conflict of interest.

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荧光纳米成像破解工业分子筛催化剂“黑箱”: 传质-酸性-积炭机理与优化设计

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摘 要: 工业分子筛催化剂(典型如 FCC 催化剂)的应用性能, 受其传质、酸性及积炭等微观行为制约。传统表征技术对此类“结构-性能”关系的认知存在局限。本综述总结了超分辨荧光成像技术在解析上述关键微观过程的最新研究进展: (1) 传质扩散行为: 揭示了反应分子在复杂等级孔道内的非均匀扩散行为; (2) 酸中心可及性: 实现了酸性位点的纳米级定位与可接近性的可视化; (3) 积炭行为: 辨识了催化剂上积炭物种的时空演变机制。同时, 还系统阐述了超分辨成像如何从纳米尺度深化对催化剂核心机理的理解, 为精准设计高性能催化剂(优化孔道、调控酸中心、抑制积炭)提供关键理论支撑, 并展望了该技术面临的挑战与未来发展方向。

关键词: 超分辨荧光成像技术; 分子筛催化剂; 传质扩散; 酸中心; 积炭

中图分类号: O657.3; TQ426.94

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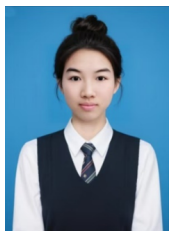
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