Application of *Operando* Spectroscopy on Catalytic Reactions

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Abstract:

This mini-review summarizes the use of *operando* spectroscopy to investigate the dynamic structure of heterogeneous catalysts under working conditions. Following the background to the development of *operando* spectroscopy, we briefly reviewed the latest highlight on this subject. Then, two challenging but attention-grabbing techniques, i.e. *operando* techniques under the harsh conditions and the integration of *operando* techniques in a unit cell, were introduced. Likely, *Operando* techniques open up new vistas to explore reaction mechanisms and help us design the next generation industrial catalysts

Keywords: *operando* spectroscopy; catalysis; dynamic structure; mechanism

1. Introduction

Catalysis is a fascinating science for those who are actively involved and even more than 85% of all fuels and chemicals are produced in catalytic processes [1]. However, the development of industrial catalysts is a costly and lengthy process because the catalytic process is still a magic box. Up to now, the catalyst R&D is mainly based on a large amount of measuring work.

In 2013, Ertl pointed out, *“Since today, we know that traditional characterization techniques can give us several supplementary evidences, but it can only provide information from fresh or spent catalysts rather than study the structure-performance relationship directly”* [2]. Likewise, the conventional approaches are not able to reveal the real structure of catalysts since the characterization is only proceeded before and after reaction. Moreover, there are three gaps between fundamental and real catalysis, the gaps of materials, pressures and complexity [3**]. Therefore, the concepts resulting from the fundamental catalysis, the basis of model catalysts in high vacuum systems, are not always applicable on the understanding of industrial catalysts. The rational design and controllable synthesis of practical catalysts are the dreamful motto desired by the catalytic fraternity.

As Schlögl declared *“In-situ investigations with complementary methods are not a ‘luxury’ but rather essential parts of the formulating a hypothesis on the function of materials”* [3**]. Among all in situ techniques, *operando* experiment is a straightforward way to determine the dynamic structure of catalysts and can offer reliable information for the rational design of catalysts by characterizing the catalytic

under realistic reaction conditions. The earliest study on *operando* technique can be dated back to 1977 by Tamara, who combined pulses of reactants with an infrared in situ cell connecting to a simultaneous gas-chromatograph to analyze the products [4]. Only after 25 years, the term “*operando*” was first introduced to emphasize on the spectroscopic measurements operated under realistic reaction conditions. A methodology that combines simultaneous in situ spectroscopy and kinetic measurements was reported [5]. *Operando* measurements, as cutting-edge techniques, allow researchers to get deep insight into the birth/get-up (activation) via the life/work (function) to the death/sleep (deactivation) and to establish a structure-performance relationship for a catalytic system [6**,7].

2. Monitoring Catalytic Reactions using *Operando* spectroscopy

To date, several spectroscopic systems, such as Raman [8*-14], UV [15-19], Infrared spectra [20-24], XRD [25*-28], X-ray adsorption [29-33] etc. have already been reassembled and operated under *operando* conditions with the advances on instruments. In accordance with the SciFinder data, for instance, *operando* Raman spectroscopy has triggered researchers high attention (by Oct. 2015, 187 papers included) because of the following factor: (1) **it is** sensitive to a tiny modification of the structure; (2) the Raman signal is less affected by the presence of H₂O and other gases; (3) it could be operated in a broad temperature range 25~1000 °C and pressure range 0.1~10.0 MPa. Using *operando* NIR-Raman, Banares and co-workers have studied the photocatalytic epoxidation of cyclohexene over V-based catalysts and

revealed that the cyclohexene was directly photo-epoxidized to 1,2-epoxycyclohexane by t-BuOOH during the reaction [34]. Li's group has monitored the synthesis process of various catalytic materials, such as Fe-, V-, Mo-based and zeolite catalysts and so on, using *operando* UV-Raman [35]. By the Surface Enhanced Raman Spectroscopy (SERS) technique, the Tian's group has explored the process of material synthesis [36]. Moreover, the Han's group has determined the near-surface structure of α -Mn₂O₃ nanocrystals during the adsorption and oxidation of CO using *operando* Raman spectroscopy. The most recent *operando* Raman work from the Wachs's group, who has a great contribution to this field, reported that surface MoO_x sites could be reduced to ordered MoO_xC_x nanoparticles when aromatics were formed during methane aromatization [37].

Using *operando* XANES and EXAFS, Weckhuysen and co-workers found that the copper species should be active sites for ethanol to butadiene over a Cu/Si/Mg catalyst [38]. The Bao's group has made several breakthroughs in the nano-confined catalysis applied for the conversion of syngas through synchrotron-based techniques [39]. Moreover, the Gaigneaux's group focuses on the synergistic mechanism for ammonia synthesis over different-sized Ru nanocatalysts [40] using *operando* DRIFTS. Tao and coworkers have studied the reconstruction of the alloy catalyst surface through the *operando* ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and ambient pressure scanning tunnel microscope (AP-STM) [41]. Nevertheless, all reported *operando* experiments, more or less, are operated under simulated reaction conditions. The data directly from those catalytic reactions, such as

syngas synthesis and ammonia synthesis, under harsh conditions (high pressure and high temperature) is still rare.

3. Challenge works in *operando* techniques

Herein, two methodologies, *operando* techniques under harsh conditions and the integration of *operando* techniques in a unit cell, are discussed to demonstrate the advantage of these methods for deeply understanding of the reaction mechanism and the origin of active sites.

3.1 *Operando* techniques under harsh conditions

The structure of catalyst has proven to be greatly affected by reaction conditions. For instance, high reaction temperature usually leads to the sintering and aggregation of individual catalyst particles and the reduction in the adsorption sites on the surfaces, thus further deteriorates the catalytic performance. Therefore, the development of *operando* techniques operating under harsh conditions is of paramount importance for the study of dynamic structures of industrial catalysts.

The *operando* Raman spectroscopy is naturally born for this aim because it is insensitive to CO₂ and H₂O in the reaction system; those species have hampered most of spectroscopy applied in *operando* measurements. More recently, as a consecutive effort, *operando* Raman spectroscopy has been used to monitor the structural evolution of iron-based catalysts in the FTS reaction at a pressure of 3.0 MPa and a temperature of 260 °C [[42**](#)], a typical industrial reaction running at harsh conditions.

FTS is regarded as one of the most important pathways for the conversion of methane (natural gas and shale gas) and coal to chemical feedstocks and fuels [[43](#)], or

to say, a clean coal technique. However, the complexity of the iron-oxide-carbide system blocks the straightforwardly correlating the dynamic structure with performance [44]. Therefore, the distinction of the real active phase(s) of the iron-based FTS catalysts is still debatable, even though tremendous efforts have been contributed in the last 100 years. Using the *operando* Raman spectroscopy (ORS), Han's group [42] has successfully determined active phases for the iron-based FTS reaction under industrial conditions. The structure of α -Fe₂O₃ catalyst was observed to experience extensive restructuring processes under activation and reaction processes (Figure 1 and Scheme 1). α -Fe₂O₃ was only partially transformed into γ -Fe₂O₃ under H₂ pretreatment and the main phase during reaction is the mixture of α -Fe₂O₃ and γ -Fe₂O₃. CO- and H₂/CO-activated catalysts showed a transformation of α -Fe₂O₃ $\rightarrow$ γ -Fe₂O₃ $\rightarrow$ Fe₃O₄ $\rightarrow$ Fe₅C₂; meanwhile Fe₃O₄ is prevailed during reaction. The catalytic activity followed an order of CO-activated > H₂/CO-activated $\approx$ H₂-activated [42]. The relationships of structure and performance suggest: (1) γ -Fe₂O₃ or Fe carbides should be responsible for its lower FTS activity; (2) Fe₃O₄ plays an important role for FTS; (3) carbonaceous species involves (positive or negative) in determining the performance of iron-based FTS catalysts.

Figure 1. *Operando* Raman spectra of α -Fe₂O₃ during the reaction processes(260°C, 3MPa) were recorded in the time interval of 30min for 7h with the flow of 3.2 mL/min, corresponding to a gas hourly space velocity(GHSV) of ca.12000 h⁻¹;(a) and (b) 10% H₂/Ar. (c) and (d) 10%CO/Ar; (e) and (f), 5%CO/5%H₂/Ar. (a), (c), (e) represent the structural evolution of the catalyst; (b), (d), (f) represent the catalytic performance, correspondingly. CO conversion (■); Selectivity of C₂-C₄ olefins(Δ)

Source: adapted from Ref.[42**]

Scheme 1. Structure evolution of hematite during both activation and reaction

processes.

Source: adapted from Ref.[[42**](#)]

3.2 Integration of *Operando* multi-techniques in one reaction

It notes that every method has limitations in practical application. For example, X-ray absorption spectroscopy (XAS) can provide information about catalysts geometric structure and electronic properties, especially the short-range structure. Albeit with exquisite spatial resolution, XAS is not able to determine the structural heterogeneity of heterogeneous materials since **it is** an ensemble-averaging characterization technique [[45,46**](#)]. On the other hand, atomic displacement in individual nanoparticles with a sub-pm precision can be measured directly using the electron microscopy, but it suffers from limited statistics and experimental artifacts associated with beam damage, insufficient resolution and/or lack of signal to noise. Therefore, it is necessary to accurately describe the complex systems with a combination of multi-techniques.

Recently, with coupling a portable micro-reactor and *operando* STEM/XAS, Jung et al [[46](#)] has correlated the structure and property of a nanoscale silica-supported Pt cluster catalyst for ethylene hydrogenation. The experimental set-up is displayed in Figure 2. The nano-catalyst is confined between two thin SiN windows separated by an integrated spacer. The material gases pass through the spacer for their reaction which underwent five steps shift, pure $H_2 \rightarrow H_2:C_2H_4 = 3:1 \rightarrow$ pure $H_2 \rightarrow H_2:C_2H_4 = 1:3 \rightarrow$ pure H_2 .

Figure 2 | Schematic of experimental cell.

Source: adapted from Ref.[[46**](#)]

With the combination of XAS (EXAFS & XANES) and STEM (Figure 3a,b and c), the catalyst was reduced in the first three steps ($\text{H}_2 \rightarrow \text{H}_2:\text{C}_2\text{H}_4=3:1 \rightarrow \text{H}_2$). However, the peak intensity of Pt increases with accompanying a blue-shift of the edge energy. Consequently, the nanoparticles in catalysts agglomerated.

Figure 3 | The experimental results from XAFS and STEM. (a) The XANES spectra, (b) the Fourier transform magnitudes of Pt L3 edge EXAFS spectra, and (c) the STEM images are shown as measured in the operando mode, during different reaction regimes.

Source: adapted from Ref.[[46**](#)]

As shown in Figure 4a, the rise in the number of small clusters at the **steps 4 and 5 did not** result from the reduction of oxidized Pt species, which could be completed at the step 3. Distributions of particle size in Figure 4b indicates that (1) the number of oxidized species gradually decreases at the step 1, (2) agglomeration of particles was observed at the step 3, while Pt particles were reduced. On the basis of these observations, the author hypothesized that the reduction of the Pt oxide species was a necessary step, which enhance the agglomeration of ultra-small clusters into larger particles. The combination of *operando* XAS and STEM can provide deep insight into the understanding of dynamic structural of catalytic materials.

Figure 4 (a) Fractions of ultra-small Pt species, sub-nm in size; (b) Evolution in number density of Pt species (schematic).

Source: adapted from Ref.[[46**](#)]

4. Perspective

The application of *operando* techniques will greatly enhance the establishment of the relationship between structure and performance of a catalyst, which is of paramount importance for the understanding of the origin of active sites and reaction pathways. Moreover, the assembly of *operando* multi-techniques in a unit system will reduce the inconsistencies in reproducibility caused by separated measurements. However, given the examples above, there is still a long way for the deep understanding of catalytic reactions, the following works are suggested:

1) To develop *operando* techniques that can probe the structure of catalysts in pilot-scale and even industrial-scale reactors so as to reveal the dynamic evolutions of catalysts under multi-scale conditions. For example, optical fibers could be used as media which can lead the laser (UV Visible or Raman laser) into the interior of

industrial reactors; by this way, no matter the gas-solid or liquid phase catalytic reactions, the structure evolution of catalysts along the catalyst bed could be probed by *operando* techniques. We believe *operando* techniques will significantly improve catalytic process by determining the catalyst structure and surface species under real industrial conditions.

2) To develop temporal-spatial resolved spectroscopy, in conjunction with the design and construction of high quality spectroscopic reaction cell applied under harsh conditions. The combination of spectroscopic and imaging techniques will deliver new and valuable insights into complex chemical problems in the design of novel and improved catalysts. Currently, *operando system*, which could measure temporal- spatial variations of catalysts with high quality, is rare to be applied under typical industrial conditions (high pressure/temperature). With the development of optics, imaging and detection techniques, the data with a higher spatial and time-resolved resolution will be achievable. We expect these *operando* techniques will be used in the design of the next generation of industrial catalysts.

3) To integrate theoretic and experimental studies. As we know, one of the major challenges in modern catalysis is the rational design of a catalyst based on the structure of active sites. Nowadays, using state-of-the-art *operando* techniques, the relationship between structure and performance of a catalyst under working conditions could be established. However, the structure changes in working catalysts and the formation of intermediates in the typical catalytic reactions are too rapid to be detected experimentally, or spectra data acquired in reactions could not be found in

the database. In this aspect, the first principles modeling is best placed to study the dynamic structure of working catalysts and validates our chemical intuition on a reaction. Breakthrough in heterogeneous catalysis will only occur when catalytic systems are fully understood. In combination with well-designed *operando* experiments on applied catalysts and first principle modelling, we believe rational design of active sites, as “a dreamful methodology”, will come true.

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6. 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. [Olah GA: **Beyond oil and gas: The methanol economy.** *Angewandte Chemie International Edition* \(2005\) **44**\(18\):2636-2639.](#)
2. [Ertl G: **Molecules at surfaces: 100 years of physical chemistry in berlin-dahlem.** *Angewandte Chemie International Edition* \(2013\) **52**\(1\):52-60.](#)
- 3.** [Schlögl R: **Heterogeneous catalysis.** *Angewandte Chemie* \(2015\) **127**\(11\):3531-3589.](#)

This review focus on the heterogeneous catalysts, the author believe a heterogeneous catalyst is a functional material that continually creates active sites with its reactant under reaction conditions. The task in this review was to demonstrate to the reader need to allow a degree of chemical complexity to enter into the rigorous world of physicochemical catalysis.

4. [Dickel G, Pitesa B: **Institut für physikalische chemie der universität münchen.** *Zeitschrift für physikalische Chemie* \(1977\) **106**:337.](#)
5. [Bañares MA: **Operando methodology: Combination of in situ spectroscopy and simultaneous activity measurements under catalytic reaction conditions.** *Catalysis today* \(2005\) **100**\(1\):71-77.](#)
- 6.** [Weckhuysen BM: **Studying birth, life and death of catalytic solids with operando spectroscopy.** *National Science Review* \(2015\) .](#)

This is another minireview about operando technology.

7. [Bañares MA: **Operando spectroscopy: The knowledge bridge to assessing structure–performance relationships in catalyst nanoparticles.** *Advanced Materials* \(2011\) **23**\(44\):5293-5301.](#)
- 8.* [Yang L, Cheng S, Ji X, Jiang Y, Zhou J, Liu M: **Investigations into the origin of pseudocapacitive behavior of Mn₃O₄ electrodes using in operando raman spectroscopy.** *Journal of Materials Chemistry A* \(2015\) **3**\(14\):7338-7344.](#)

In this paper, the authors probed the phases changes of Mn₃O₄ electrode material in a pseudocapacitor during a charging and discharging process using operando Raman spectroscopy. A detailed understanding of the phase changes of manganese oxides in the pseudocapacitor during cycling is vital to reveal the mechanism and to achieve a rational design of improved electrode materials.

9. [Sattler JJ, Mens AM, Weckhuysen BM: **Real - time quantitative operando raman spectroscopy of a crox/Al₂O₃ propane dehydrogenation catalyst in a pilot - scale reactor.** *ChemCatChem* \(2014\) **6**\(11\):3139-3145.](#)
10. [Deabate S, Huguet P, Morin A, Gebel G, Lanteri Y, Peng Z, Sutor AK: **Raman microspectroscopy as a useful tool for in situ and operando studies of water transport in perfluorosulfonic membranes for pemfcs.** *Fuel Cells* \(2014\) **14**\(5\):677-693.](#)
11. [Xu J, Deng Y-Q, Zhang X-M, Luo Y, Mao W, Yang X-J, Ouyang L, Tian P, Han Y-F: **Preparation, characterization, and kinetic study of a core–shell Mn₃O₄@ SiO₂ nanostructure catalyst for co oxidation.** *ACS Catalysis* \(2014\) **4**\(11\):4106-4115.](#)
- 12.* [Xu J, Deng Y-Q, Luo Y, Mao W, Yang X-J, Han Y-F: **Operando raman spectroscopy and kinetic study of low-temperature CO oxidation on an α-Mn₂O₃ nanocatalyst.** *Journal of Catalysis* \(2013\) **300**\(225-234.](#)

With the combination of the temperature programmed desorption of O₂, temperature

programmed surface reaction of CO oxidation, *operando* Raman and kinetics parameters, the author found that the oxidation of CO may proceed with different mechanisms under different temperatures.

13. [Luo Y, Deng Y-Q, Mao W, Yang X-J, Zhu K, Xu J, Han Y-F: **Probing the surface structure of \$\alpha\$ -Mn₂O₃ nanocrystals during co oxidation by *operando* Raman spectroscopy.** *The Journal of Physical Chemistry C* \(2012\) **116**\(39\):20975-20981.](#)
14. [Xu J, Ouyang L, Mao W, Yang X-J, Xu X-C, Su J-J, Zhuang T-Z, Li H, Han Y-F: **Operando and kinetic study of low-temperature, lean-burn methane combustion over a Pd/ \$\gamma\$ -Al₂O₃ catalyst.** *ACS Catalysis* \(2012\) **2**\(2\):261-269.](#)
15. [Sattler J, Gonzalez-Jimenez I, Mens A, Arias M, Visser T, Weckhuysen B: **Operando UV-Vis spectroscopy of a catalytic solid in a pilot-scale reactor: Deactivation of a \$\gamma\$ -Al₂O₃ propane dehydrogenation catalyst.** *Chemical Communications* \(2013\) **49**\(15\):1518-1520.](#)
16. [Qian Q, Vogt C, Mokhtar M, Asiri AM, Al-Thabaiti SA, Basahel SN, Ruiz-Martínez J, Weckhuysen BM: **Combined *operando* UV/Vis/IR spectroscopy reveals the role of methoxy and aromatic species during the methanol-to-olefins reaction over SAPO-34.** *ChemCatChem* \(2014\) **6**\(12\):3396-3408.](#)
17. [Kondratenko EV, Takahashi N, Nagata N, Ibe M, Hirata H, Takahashi H: **Operando UV/Vis analysis of the synergy effect between copper and gold in nitric oxide reduction over gold and copper on alumina catalysts.** *ChemCatChem* \(2015\).](#)
18. [Patel MU, Dominko R: **Application of in *operando* UV/Vis spectroscopy in lithium–sulfur batteries.** *ChemSusChem* \(2014\) **7**\(8\):2167-2175.](#)
19. [Patel MU, Demir - Cakan R, Morcrette M, Tarascon JM, Gaberscek M, Dominko R: **Li-s battery analyzed by UV/Vis in *operando* mode.** *ChemSusChem* \(2013\) **6**\(7\):1177-1181.](#)
20. [Wuttke S, Bazin P, Vimont A, Serre C, Seo YK, Hwang YK, Chang JS, Férey G, Daturi M: **Discovering the active sites for C₃ separation in mil-100 \(Fe\) by using *operando* IR spectroscopy.** *Chemistry-A European Journal* \(2012\) **18**\(38\):11959-11967.](#)
21. [Aldana PU, Ocampo F, Kobl K, Louis B, Thibault-Starzyk F, Daturi M, Bazin P, Thomas S, Roger A: **Catalytic CO₂ valorization into CH₄ on Ni-based ceria-zirconia. Reaction mechanism by *operando* IR spectroscopy.**](#)

Catalysis Today (2013) **215**(201-207).

22. Dupré J, Bazin P, Marie O, Daturi M, Jeandel X, Meunier F: **Understanding the storage function of a commercial nox-storage-reduction material using operando IR under realistic conditions.** *Applied Catalysis B: Environmental* (2014) **160** 335-343.
 23. Vilmin F, Bottero I, Travert A, Malicki N, Gaboriaud F, Trivella AI, Thibault-Starzyk Fdr: **Reactivity of bis [3-(triethoxysilyl) propyl] tetrasulfide (tespt) silane coupling agent over hydrated silica: OperandoIR spectroscopy and chemometrics study.** *The Journal of Physical Chemistry C* (2014) **118**(8):4056-4071.
 24. Kaftan A, Kollhoff F, Nguyen T-S, Piccolo L, Laurin M, Libuda J: **Sensitivity of CO oxidation toward metal oxidation state in ceria-supported catalysts: An operando DRIFTS-MS study.** *Catalysis Science & Technology* (2015).
 - 25.* Hess M, Sasaki T, Villevieille C, Novák P: **Combined operando X-ray diffraction-electrochemical impedance spectroscopy detecting solid solution reactions of lifepo4 in batteries.** *Nature communications* (2015) **6**:8169
- In this paper, the author reported that the combination of high-resolution *operando* synchrotron X-ray diffraction and electrochemical impedance spectroscopy could directly track non equilibrium intermediate phases in lithium-ion battery materials.
26. Gaubicher J, Boucher F, Moreau P, Cuisinier M, Soudan P, Elkaïm E, Guyomard D: **Abnormal operando structural behavior of sodium battery material: Influence of dynamic on phase diagram of na x fepo 4.** *Electrochemistry Communications* (2014) **38** 104-106.
 27. Sougrati MT, Fullenwarth J, Debenedetti A, Fraisse B, Jumas J-C, Monconduit L: **Tisnsb a new efficient negative electrode for li-ion batteries: Mechanism investigations by operando-XRD and mössbauer techniques.** *Journal of Materials Chemistry* (2011) **21**(27):10069-10076.
 28. Waluś S, Barchasz C, Bouchet R, Lepître JC, Colin JF, Martin JF, Elkaïm E, Baecht C, Alloin F: **Lithium/sulfur batteries upon cycling: Structural modifications and species quantification by in situ and operando X-ray diffraction spectroscopy.** *Advanced Energy Materials* (2015).
 29. Mutz B, Carvalho HW, Mangold S, Kleist W, Grunwaldt J-D: **Methanation of CO₂: Structural response of a Ni-based catalyst under fluctuating reaction conditions unraveled by operando spectroscopy.** *Journal of Catalysis* (2015)

[327:48-53.](#)

30. [O'Neill BJ, Miller JT, Dietrich PJ, Sollberger FG, Ribeiro FH, Dumesic JA: **Operando X-ray absorption spectroscopy studies of sintering for supported copper catalysts during liquid-phase reaction.** *ChemCatChem* \(2014\) 6\(9\):2493-2496.](#)
31. [Bora DK, Glans P-A, Pepper J, Liu Y-S, Du C, Wang D, Guo J-H: **An ultra-high vacuum electrochemical flow cell for in situ/operando soft X-ray spectroscopy study.** *Review of Scientific Instruments* \(2014\) 85\(4\):043106.](#)
32. [Bagg-Hansen M, Wood BC, Ogitsu T, Willey TM, Tran IC, Wittstock A, Biener MM, Merrill MD, Worsley MA, Otani M: **Potential-induced electronic structure changes in supercapacitor electrodes observed by in operando soft X-ray spectroscopy.** *Advanced Materials* \(2015\) 27\(9\):1512-1518.](#)
33. [Shin J, Kim M, Cirera J, Chen S, Halder GJ, Yersak TA, Paesani F, Cohen SM, Meng YS: **Mil-101 \(Fe\) as a lithium-ion battery electrode material: A relaxation and intercalation mechanism during lithium insertion.** *Journal of Materials Chemistry A* \(2015\) 3\(8\):4738-4744.](#)
34. [Chan H-Y, Nguyen V-H, Wu J, Calvino-Casilda V, Bañares MA, Bai H: **Real-time raman monitoring during photocatalytic epoxidation of cyclohexene over V-Ti/MCM-41 catalysts.** *Catalysts* \(2015\) 5\(2\):518-533.](#)
35. [Jin S, Feng Z, Fan F, Li C: **UV raman spectroscopic characterization of catalysts and catalytic active sites.** *Catalysis Letters* \(2015\) 145\(1\):468-481.](#)
36. [Lin L, Tian X, Hong S, Dai P, You Q, Wang R, Feng L, Xie C, Tian ZQ, Chen X: **A bioorthogonal raman reporter strategy for SERS detection of glycans on live cells.** *Angewandte Chemie* \(2013\) 125\(28\):7407-7412.](#)
37. [Wachs IE: **An operando molecular spectroscopic and density function theory \(DFT\) calculation investigation of methane aromatization by supported Mo/ZSM-5 catalysts.**](#)
38. [Angelici C, Meirer F, van der Eerden AM, Schaink HL, Goryachev A, Hofmann JP, Hensen EJ, Weckhuysen BM, Bruijninx PC: **Ex situ and operando studies on the role of copper in Cu-promoted SiO₂-MgO catalysts for the lebedev ethanol-to-butadiene process.** *ACS Catalysis* \(2015\) 5:6005-6015.](#)

39. [Chen W, Fan Z, Pan X, Bao X: **Effect of confinement in carbon nanotubes on the activity of Fischer–Tropsch iron catalyst.** *Journal of the American Chemical Society* \(2008\) **130**\(29\):9414-9419.](#)
40. [Fernández C, Pezzotta C, Gaigneaux EM, Bion N, Duprez D, Ruiz P: **Disclosing the synergistic mechanism in the catalytic activity of different-sized Ru nanoparticles for ammonia synthesis at mild reaction conditions.** *Catalysis Today* \(2015\) **251**\(88-95\).](#)
41. [Tao FF, Salmeron M: **In situ studies of chemistry and structure of materials in reactive environments.** *Science* \(2011\) **331**\(6014\):171-174.](#)
- 42.** [Fu D, Dai W, Xu X, Mao W, Su J, Zhang Z, Shi B, Smith J, Li P, Xu J, Han Y: **Probing the structure evolution of iron - based Fischer - Tropsch to produce olefins by operando raman spectroscopy.** *ChemCatChem* \(2015\) **7**\(5\):752-756.](#)

By using *operando* raman spectroscopy, the author investigated the panoramic structure evolution of an iron oxide catalyst, which is used for the production of olefins via Fischer-Tropsch. Such a study is critical for further understanding of different catalytic reactions.

43. [Galvis HMT, Bitter JH, Khare CB, Ruitenbeek M, Dugulan AI, de Jong KP: **Supported iron nanoparticles as catalysts for sustainable production of lower olefins.** *Science* \(2012\) **335**\(6070\):835-838.](#)
44. [de Smit E, Weckhuysen BM: **The renaissance of iron-based fischer-tropsch synthesis: On the multifaceted catalyst deactivation behaviour.** *Chemical Society reviews* \(2008\) **37**\(12\):2758-2781.](#)
45. [Jung U, Elsen A, Li Y, Smith JG, Small MW, Stach EA, Frenkel AI, Nuzzo RG: **Comparative in operando studies in heterogeneous catalysis: Atomic and electronic structural features in the hydrogenation of ethylene over supported pd and pt catalysts.** *ACS Catalysis* \(2015\) **5**\(3\):1539-1551.](#)
- 46.** [Li Y, Zakharov D, Zhao S, Tappero R, Jung U, Elsen A, Baumann P, Nuzzo RG, Stach E, Frenkel A: **Complex structural dynamics of nanocatalysts revealed in operando conditions by correlated imaging and spectroscopy probes.** *Nature communications* \(2015\) **6**:7583](#)

In this paper, by a co-registered use of synchrotron X-ray absorption spectroscopy and scanning transmission electron microscopy in *operando* conditions, the author quantitatively described the complex structural dynamics of supported Pt catalysts during catalytic reaction.