A combined *in operando* approach for low-energy Scanning Transmission Electron Microscopy and Grazing Incident Small Angle X-ray Scattering

Simone Dal Zilio,[1] Marc Salleras,[2] Lluis Balcells,[2] Jaume Esteve,[2] Raju Edla,[1] Allison P. Young,[3] Chia-Kuang Tsung,[3] Paolo Scardi,[4] Reza Rashidi,[5] Giuseppe Cautero,[5] Benedetta Marmiroli,[6,7] Heintz Amenitsch,[6,7] Regina Ciancio[1]

[1]*CNR-IOM TASC, Area Science Park Basovizza, Trieste, Italy*
[2]*IMB-CNM (CSIC), Campus UAB, Bellaterra, Spain*
[3]*Boston College, Merkert Chemistry Center, Department of Chemistry, Chestnut Hill, MA, USA*
[4]*Department of Civil, Environmental & Mechanical Engineering, University of Trento, Italy*
[5]*Elettra-Sincrotrone Trieste S.C.p.A, Area Science Park Basovizza, Trieste, Italy*
[6]*Institute of Inorganic Chemistry, Graz University of Technology, Graz, Austria*
[7]*Austrian SAXS Beamline at ELETTRA, Trieste, Italy*

Corresponding author: Simone Dal Zilio, CNR-IOM TASC, Area Science Park Basovizza, S.S. 14 Km 163.5, 34149 Trieste, Italy. Tel. +39.040.3756467 – Fax: +39.040.226767. E-mail: dalzilio@iom.cnr.it

Key words: STEM; *in operando*; GISAXS; catalysts; microreactor.

Acknowledgments: This work is supported by the European Research Infrastructure NFFA-Europe, funded by EU's H2020 framework program for research and innovation under grant agreement n. 654360.

SUMMARY

Probing the evolution of electronic, structural, and chemical properties of nanostructured materials under reaction conditions is a crucial issue to determine their structure-functionality relationships. A relevant example is represented by heterogeneous catalysts, whose properties change dramatically with respect to the environment. Much of effort has been made lately in designing new solutions and technologies, or modifying the existing ones for purpose of *operando* conditions analysis. The use of micro- or nanoreactors is a second approach, where ultrathin membranes can efficiently separate the high-pressure volume from the (ultra)high vacuum of the characterization chamber. Very recently, microreactor cells have been developed to integrate the capabilities of ensemble-averaging synchrotron techniques with local probe ones, as TEM to analyze the same catalytic process with different instruments. Despite the great power of this method, the extremely small probing size of TEMs restricts the application of a combined approach to a limited set of micro-focused synchrotron techniques.

We propose here the development of a novel multifunctional microreactor for *operando* low voltage Scanning TEM in a SEM compatible with a broad range of synchrotron techniques.

We successfully designed a device compatible with Grazing Incident Small Angle X-ray Scattering (GISAXS), demonstrating the feasibility of our approach by studying the shape and size evolution of PVP-capped Pd nanocrystals under oxidation/reaction conditions.

Received for publication: 4 September 2018. Accepted for publication: 6 September 2018.

microscopie 2018; 15:7803
doi:10.4081/microscopie.2018.7803

Introduction

The study of gas-solid reactions in nanostructured materials has gained a wide interest in the last decade. A relevant example is represented by heterogeneous catalysts where the ability to control their chemical states plays a crucial role in tuning the wealth of technological applications they can display (Tao and Crozier, 2016; Meier *et al.*, 2012; Kalz *et al.*, 2017). In this regard, probing the evolution of electronic, structural, and chemical changes in catalytic materials at *operando* conditions, would be fundamental to shed light on the interconnections between their structures and functionalities at the nanoscopic level and to tune their chemical reactions to improve catalytic performances.

The importance of *operando* characterization is now broadly accepted and, to this aim, a wide range of techniques and modes of experiments have been developed in the latest years mostly relying on synchrotron-based techniques and on the use of portable microreactors able to separate the sample environment from the UHV conditions of the working instrument (Fottinger *et al*, 2011; Kulisch *et al*, 2014; Tinnemans *et al.*, 2005; Vamvakeros *et al.*, 2015). In fact, the low-scattering cross-sections of photons with matter allow deep penetration into materials and considerably simplify the types of reactor designs to be employed for *operando* characterization in different environments, including ambient pressure conditions. Nevertheless, *operando* experiments under ambient or even harsh reaction conditions with techniques such as Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), and X-ray Microscopy (XRM), able to provide information with greater spatial resolution and to directly image the evolution of the studied phenomena, are more challenging to perform because of the extremely limited travelling distance of electrons, in the case of TEM and XPS, through moderate-pressure or even low-vacuum atmospheres.

Usually, the problem is exceeded by performing experiments at gas pressures of a few millibars through the use of a differential pumping in the system. Unfortunately, in most of these cases it is not possible to reach ambient pressure conditions, where many catalysts find technological applications, strongly affect the behavior of this materials. Bridging this so-called "*pressure gap"* is therefore crucial to clarify how the structural response of the catalytic systems at lower pressures relates to their dynamic behavior at ambient pressure conditions. Moreover, it has been demonstrated that a multiple probes approach is strongly required to characterize complementary attributes of the catalytic systems (Xu *et al.*, 2012; Tao, 2012; Patlolla *et al.,* 2013). Intensive efforts have been therefore made in the latest years to design cell microreactors working at different pressures and compatible with different experimental techniques for a multidisciplinary characterization in identical chemical conditions. A remarkable example in this respect is represented by a recently developed correlated approach to combine the capabilities of ensemble-averaging characterization techniques (XANES and IR spectroscopy, for example) with local probe techniques such as TEM to analyze the same processes by using different instruments under identical reaction conditions based on enclosed cell microreactors nowadays commercially available (Creemer *et al.*, 2008; Zhao *et al.*, 2015). Despite the power of this approach, the intrinsic heterogeneity of catalytic materials poses a considerable challenge when the reaction volumes employed in different analysis setup are extremely dissimilar. In most of synchrotron techniques, the average measurement on the specimen is collected over extended areas (hundreds of µm or more), while extremely small probing areas (a few µm) are employed in TEM, giving the possibility to acquire information on structural heterogeneity of the individual nanoparticles. Confined microreactors optimized for TEM and compatible with micro-focused spectroscopy techniques (Li *et al.*, 2015; Baier *et al.*, 2016) have been proposed, providing an integrated device for cross-linked experiments: on the other side, they can be applied just for a limited set of techniques, raising moreover questions on the effect of small reaction volumes, involved in such a device, in the catalytic reactions studied. In addition, TEM can suffer from limited statistics and experimental artifacts associated with beam damage.

We propose here a novel approach aimed to provide a novel multifunctional microreactor optimized for *operando* Scanning TEM (STEM) performed in low voltage in the Scanning Electron Microscope (SEM), but compatible with a broad range of synchrotron spectroscopy techniques. The low voltage STEM imaging in the SEM, indeed, has a series of advantages: i) if reduced electron energy is employed (up to 30 kV in most of the commercial SEMs), the cross section for light elements becomes comparable to that of conventional transmission electron microscopy observations; ii) lower modification in the sample respect the TEM or SEM mode induced by energy loss and/or charge build-up; iii) the great efficiency of the available STEM detector, giving the possibility of reduction of the total impinging radiation; iv) low degradation of images due to chromatic aberration also at low electron energy; v) the flexibility (and size) of the SEM chamber which allows the use of larger microreactors compatible with a broad range of synchrotron radiation-based techniques.

The microreactor is also conceived to be compatible with Grazing Incident Small Angle X-ray Scattering (GISAXS) and Wide-angle X-ray scattering (GIWAXS). The approach provides a great opportunity to couple the information attainable at the nanoscale level by STEM and to analyze

their collective behavior over extended areas by SAXS/WAXS. GISAXS can provide structural information on size, shape and size distribution, while synchrotron WAXS allows following changes in the crystalline structure of the sample.

Preliminary tests to ascertain the feasibility of this approach have been done to study the stability, shape and size evolution of PVP-capped Pd nanocrystals. A critical aspect in the practical applications in Pd nanocrystals (important noble metal employed in heterogeneous catalysis for chemical synthesis, fuel cells, and hydrogen storage) is in fact the shape-control and stability under ambient conditions.

Materials and Methods

The design of the device is based on a previous concept we have developed for *in situ* X-ray microscopy in liquid environment (Bozzini *and Bocchetta,* 2015), such as a sealed chamber consisting of two facing semi-transparent windows of nanometric thickness allowing the transmission of both electrons and X-rays. Despite many materials have been considered for the thin membranes (*i.e.*, graphene or polymers), SiN is the material providing the highest performance, in term of transparency to X-rays and electrons, and of mechanical properties (Ramachandra *et al.*, 2011).

The device (Figure 1) consists of two symmetrical 20 x 25 mm^2 silicon chip both having two windows of 500 nm-thick SiN membranes produced by Low Pressure Chemical Vapor Deposition (LPCVD). A 1 x 10 mm window is designed to allow the transmission of X-rays beam for GISAXS characterization, while a 0.7 x 0.7 mm window is devoted to the STEM imaging. Although 500 nm thick membranes have been proved to be suitable to limit hard X-ray photon absorption employed in SAXS experiments, thinner membranes are necessary to allow electron transparency, in particular for reduced electron energy used for STEM imaging. Nevertheless, ultrathin membranes put high demands on their mechanical resistance when a pressure difference of 1 bar is applied towards the vacuum of the STEM chamber, becoming even more critical when extended transparent windows are needed to couple between techniques like STEM and SAXS.

To ensure electron transparency while preserving mechanical resistance of the membranes, the smaller window was patterned to produce ultrathin (up to 30 nm) SiN membrane in micro-windows 10 µm wide in diameter: the patterning has been defined, matching the maximum tolerable stress/displacement when a pressure difference of 1 bar is applied towards the vacuum of the STEM chamber (Figure 2), and an adequate area for imaging. The transparency respect the SiN thickness in the thinned windows has been evaluated experimentally monitoring the quality of the STEM images of Pd nanoparticles increasing the thinning. In Figure 3 it is possible to appreciate the difference in STEM images varying the total thickness of the windows. The estimation of the transmission of the membranes in respect to their thickness has been investigated by inserting the nanoparticles in between two chips having the same SiN thick windows. We employed a 30 kV acceleration voltage, the maximum available for the SEM used for the present work (Zeiss Supra 40 equipped with 4-Channel-aSTEM Detector). No gas was injected for this preliminary characterization. The quality of the obtained images has been eval-

Figure 1. A) 3D sketch of the proposed device, showing the two windowed faced silicon chips. B) Representation of the device inserted in the holder designed for the fitting in both SAXS and STEM setup. C) A picture of the holder showing the tubes for the gas injection inside the cell.

uated comparing an image of the same nanoparticles deposited on standard TEM grids. 30 nm was the maximum SiN thickness for good quality images, allowing to monitor the shape and size changes in *operando* conditions. The patterning and thinning of the membranes have been performed by suitable top-down approach, consisting in a first UV-lithography step to define the micrometric dots array centered in the small windows followed by the transfer in a thin Cr thin layer by wet etching process. An ICP-RIE (STS) dry etching recipe, with optimal control of uniformity and etching rate, is then employed to transfer the pattern in the SiN film up to reach the desired residual thickness. The whole process has been optimized to prevent membranes from damages and local cracks in the thinned layer.

The top chip contains the integrated inlets for gas injection; the flow of the reaction gasses through the microreactor is obtained by a controlled spacing (from 1 to 5 µm). A microfluidic channel is produced by classical UV-lithography and replica molding in a suitable polymeric material (OSTE+) (Pardon *et al.*, 2014): it guarantees also the correct sealing of the cell and permits the cell to be opened for the experiments in the SAXS beamline. The diffused methods employing permanent sealing of the cell, employing polymeric resins, metal or silicon-based bonding (Grogan and Bau, 2011), although highly efficient and simple to fabricate, were discarded: the reasons are basically the possibility to perform experiments in open configuration and to have higher flexibility in sample deposition, *i.e.* in the case of Pd nanoparticles, drop casting or spin coating, to have better control in catalyst distribution on the membrane surface.

The bottom chip contains the integrated MEMS heater, schematically shown in Figure 4: it consists in a series of tungsten traces aligned on both the membranes. Different size and distribution have been designed and employed for large and small windows in order to have the lowest interfer-

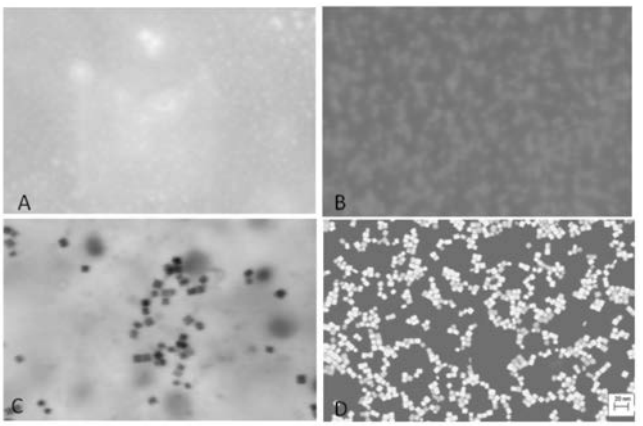

Figure 3. STEM image of 10 nm Pd nanoparticles with a total SiN thickness of 200 nm (A), 100 nm (B) and 70 nm (C). D) reference image of the nanoparticles deposited on a TEM grid.

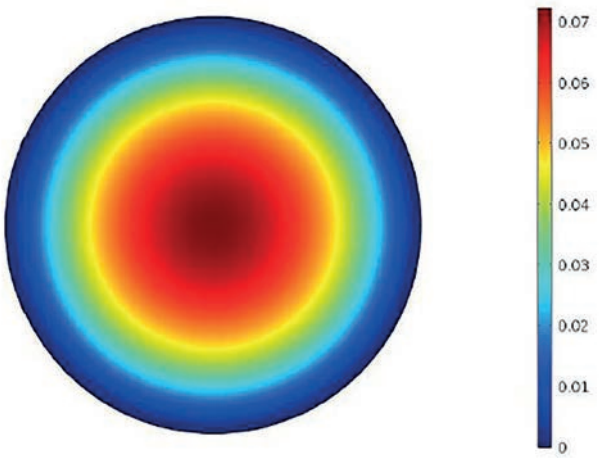

Figure 2. Membrane displacement a silicon nitride membrane with a diameter of 10 µm and a thickness of 10 nm.

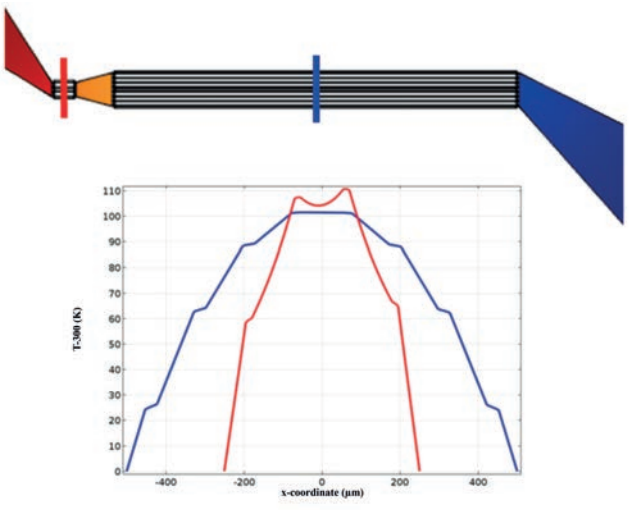

Figure 4. Schematic representation of the heater designed for the microreactor (upper drawing) and simulation of the temperature distribution (lower graph) in both the windows, STEM (red) and GISAXS (blue).

ence with GISAXS acquisition while preserving the uniformity of the temperature in every region of the microreactor. In Figure 3B, the results of the preliminary simulation are presented: as it is clearly visible, this geometry allows to obtain the good distribution of the temperature all over the cell windows.

Monitoring of the temperature was achieved by measuring the variation of the resistance induced by the heating, and converting it trough the following relation:

$$R(T)=R(T_0)(1+\alpha\Delta T)$$

where α is the constant known as the temperature coefficient of resistance (TCR), representing the resistance change factor per degree of temperature change. The TCR is achieved after suitable calibration and employed in a specifically designed LabView® program, implemented in order to finely control the heater, to avoid uncontrolled heating effect that can produce the SiN membrane braking.

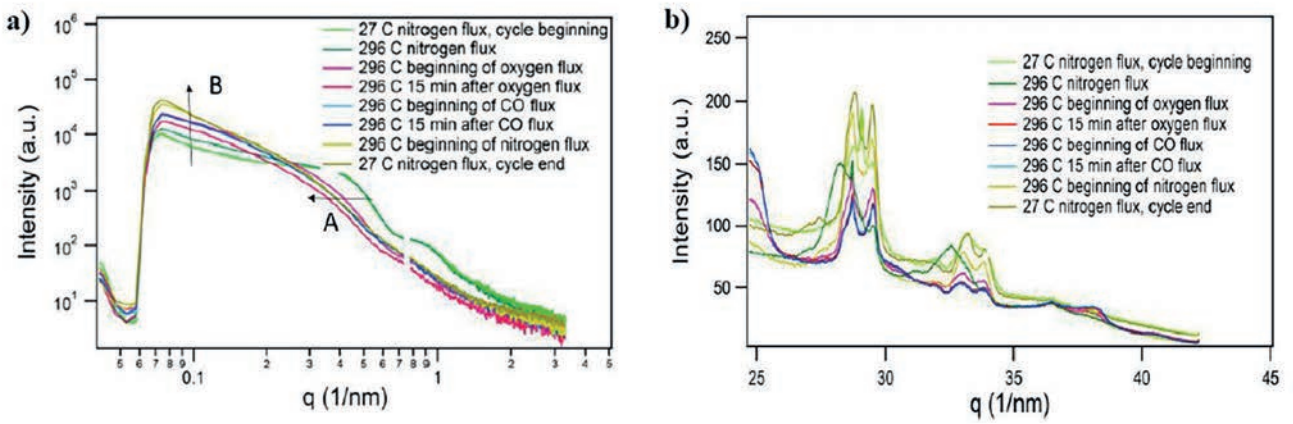

Figure 5. a) Horizontal cuts of the GISAXS pattern of the temperature cycle: N2 → O2 → CO → N2. The reported curves represent: the initial one; after the end of the heating ramp under nitrogen flow; the beginning and the end of oxygen flow; the beginning and the end of CO flow; the beginning and the end of the cooling ramp under nitrogen flow. b) WAXS data for the same conditions.

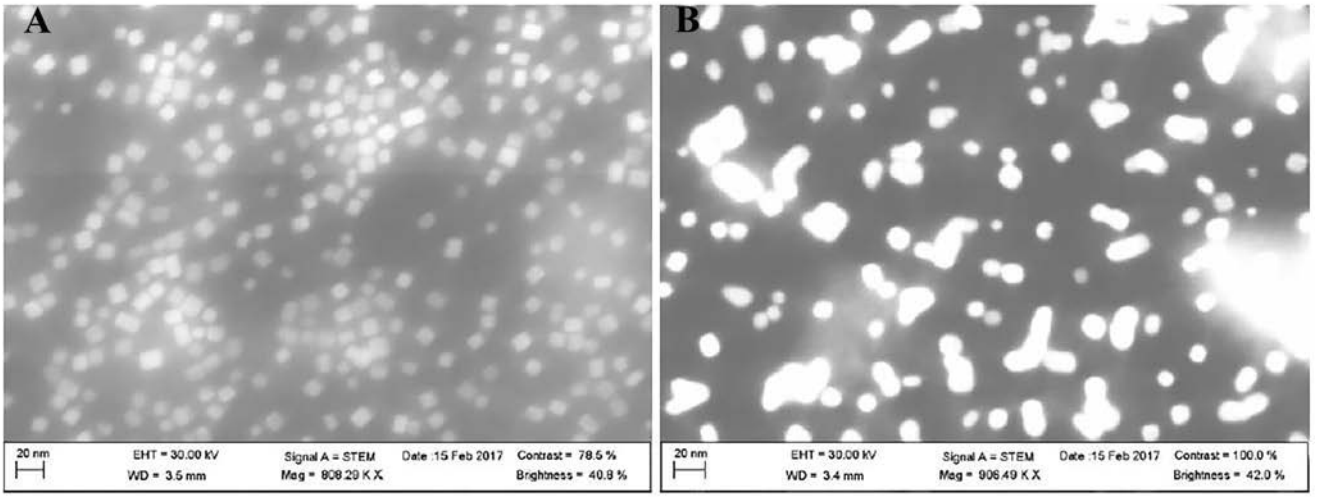

Figure 6. Dark field STEM images of synthesized Pd nanocrystals (A), and Pd nanocrystals after annealing in O_2 (B).

Results and Discussion

PVP-capped shape- controlled Pd nanoparticles of 10 nm were studied as a model sample to study the feasibility of the cell for both SAXS, performed at the Austrian SAXS beamline In Elettra, Trieste of TUG and STEM experiments, performed at CNR-IOM in Trieste. The nanoparticles were suitably drop or spin casted on the bottom membrane, to obtain a thin and homogeneous monolayer of nanoparticles and to reduce particles agglomeration. The preliminary GISAXS data of the Pd crystals deposited in the cell and exposed cyclically to temperature up to 300°C and oxygen and nitrogen flow, are presented in Figure 5. In the case of annealing in presence of N_2, no evident differences are present in the collected spectra, as we expected. When O_2 is injected into the system, a change in nanoparticle morphology is observed: the increase in particle size suggests the tendency to form bigger aggregates. On the contrary, no changes in size have been noticed during the addition of CO gas. The same behavior has been observed during the cooling under N_2. The GIWAXS pattern (Figure 5, right panel) shows distinct changes similar to the one observed during the addition of O_2. STEM analyses were performed by using a STEM/SEM operated at 30 kV. A representative dark field STEM image of synthesized Pd nanocrystals is shown in Figure 6, left panel. The nanocrystals are mostly characterized by a cubic shape with an average size of 10 nm; no significant evidence of aggregation has been observed. Considerable changes have been noticed for the sample annealed in O_2: most of the nanocrystals show an evident transition from the cubic to a spherical shape accompanied, in some case, by occurrence of aggregation.

Conclusions

A new flowing microreactor was developed to combine *operando* STEM and GISAXS experiments. We developed a suitable protocol for the fabrication of a cell consisting of facing SiN membranes allowing suitable electron transparency for STEM investigations and of extended size for GISAXS measurements. We demonstrated the achievement of the optimal electron transparency of the membranes for STEM experiments. The heating at a temperature range from 0 to 300°C is provided by a miniaturized MEMS heater, fitting the geometry of the microreactor cell without affecting the measurements performed with SAXS and STEM. This approach features a cell design that enables the possibility of combined studies for, essentially, any catalytic reaction under *operando* conditions.

References

Baier S, Wittstock A, Damsgaard CD, Diaz A, Reinhardt J, Benzi F, et al. Influence of gas atmospheres and ceria on the stability of nanoporous gold studied by environmental electron microscopy and: In situ ptychography. RSC Adv 2016;6:83031-43.

Bozzini B, Bocchetta P. In situ soft x-ray fluorescence and absorption microspectroscopy: A study of Mn-Co/polypyrrole electrodeposition. J Vac Sci Technol A 2015;33:031102.

Creemer JF, Helveg S, Hoveling GH, Ullmann S, Molenbroek AM, Sarro PM, et al. Atomic-scale electron microscopy at ambient pressure. Ultramicroscopy 2008;108:993-8.

Föttinger K, Van Bokhoven JA, Nachtegaal M, Rupprechter G. Dynamic structure of a working methanol steam reforming catalyst: in situ Quick-EXAFS on Pd/ZnO nanoparticles. J Phys Chem Lett 2011;2:428-33.

Grogan J, Bau H. In situ liquid cell TEM/STEM with the Nanoaquarium. Microsc Microanal 2011;17:532-3.

Kalz KF, Kraehnert R, Dvoyashkin M, Dittmeyer R, Gläser R, Krewer U, et al. Future challenges in heterogeneous catalysis: understanding catalysts under dynamic reaction condition. Chem Cat Chem 2017;9:17-29.

Kulisch J, Sommer H, Brezesinski T, Janek J. Simple cathode design for Li-S batteries: Cell performance and mechanistic insights by in operando X-ray diffraction. Phys Chem Chem Phys 2014;16:18765-71.

Li Y, Zakharov D, Zhao S, Tappero R, Jung U, Elsen A, et al. Complex structural dynamics of nanocatalysts revealed in Operando conditions by correlated imaging and spectroscopy probe. Nat Comm 2015;6:7583.

Meier JC, Galeano C, Katsounaros I, Topalov AA, Kostka A, Schüth F, et al. Degradation mechanisms of Pt/C fuel cell catalysts under simulated start-stop conditions. ACS Catalysis 2012;2:832-43.

Pardon G, Saharil F, Karlsson JM, Supekar O, Carlborg CF, van der Wijngaart W, et al. Rapid mold-free manufacturing of microfluidic devices with robust and spatially directed surface modifications. Microfluid Nanofluid 2014;17:773-9.

Patlolla A, Baumann P, Xu W, Senanayake SD, Rodriguez JA, Frenkel AI. Characterization of metal-oxide catalysts in Operando conditions by combining x-ray absorption and Raman spectroscopies in the same experiment. Top Catal 2013;56:896-904.

Ramachandra R, Demers H, de Jonge N. Atomic-resolution scanning transmission electron microscopy through 50-nm-thick silicon nitride membranes. App Phys Lett 2011;98:093109.

Tinnemans SJ, Kox MHF, Nijhuis TA, Visser T, Weckhuysen BM. Real time quantitative Raman spectroscopy of supported metal oxide catalysts without the need of an internal standard. Phys Chem Chem Phys 2005;7:211-6.

Tao F. Operando studies of catalyst surfaces during catalysis and under reaction conditions: ambient pressure x-ray photoelectron spectroscopy with a flow-cell reactor. Chem Cat Chem 2012;4:583-90.

Tao F, Crozier PA. Atomic-scale observations of catalyst structures under reaction conditions and during catalysis. Chem Rev 2016;116:3487-539.

Xu W, Si R, Senanayake SD, Llorca J, Idriss H, Stacchiola D, et al. In situ studies of CeO_2-supported Pt, Ru, and Pt–Ru alloy catalysts for the water–gas shift reaction: Active phases and reaction intermediates. J Catal 2012;291:117-26.

Vamvakeros A, Jacques SDM, Middelkoop V, Di Michiel M, Egan CK, Ismagilov IZ, et al. Real time chemical imaging of a working catalytic membrane reactor during oxidative coupling of methane. Chem Commun 2015;51:12752-5.

Zhao S, Li Y, Stavitski E, Tappero R, Crowley S, Castaldi MJ, et al. Operando characterization of catalysts through use of a portable microreactor. Chem Cat Chem 2015;7:3683-91.