2118
doi:10.1017/S1431927622008200
Microsc. Microanal. 28 (Suppl 1), 2022

Integration of Gas-Cell TEM, Nano-calorimetry and RGA on Oscillating Phenomena at High Temperatures in Catalysis

Dan Zhou[1*], Ronald G. Spruit[1], Merijn Pen[1], Tian Qin[2], Xiaoben Zhang[3], Fan Zhang[3], Xi Liu[2], Wei Liu[3], Hugo Perez Garza[1]

[1] DENSsolutions B.V., Delft 2628 ZD, The Netherlands
[2] School of Chemistry and Chemical Engineering, In-situ Center for Physical Sciences, Shanghai Jiaotong University, Shanghai, 200240, China
[3] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, Dalian, China.
* Corresponding author: dan.zhou@denssolutions.com

Catalysts play important roles in improving energy efficiency and developing new strategies for clean energy. Operando gas and heating TEM, integrating gas-cell TEM, nano-calorimetry and residual gas analyzer (RGA), is attracting more and more research interests in the catalysis community for its capabilities in correlating the materials' gas environment, atomic structure and reaction products at high spatial and temporal resolutions [1-3]. In this work, we will present the investigations on two oscillatory behaviors in catalyst materials with the correlated information achieved from the operando gas and heating TEM. One is the methane combustion period and amplitude oscillations catalyzed by Pd nanoparticles. The other is the NiAu nanoparticles structure and composition oscillations under hybrid dry gas and water vapor environment, which works for water gas shift reactions.

DENSsolutions' Climate G+ system, gas and heating Nano-Reactor, gas analyzer, and a FEI Titan (TEM) operated at 300 kV were used in this work. Both Pd and NiAu nanoparticles were firstly dissolved in ethanol and then transferred to the Climate nano-reactor by drop-casting.

As shown in Figure 1(a), the Nano-Reactors based on microelectromechanical systems (MEMS) make it possible to increase the pressure around the specimen to more than 2 atmospheric pressure and heat the specimen up to 1000 ^{0}C while maintaining the high vacuum in the other parts of TEM, i.e. the ex-situ TEM capabilities are conserved. Figure 1(b) shows a typical HAADF STEM image from a time-series image stack acquired with oxygen concentration changed in a continuous way. The time-series movie started with oxygen to methane 1:1 and decreased as time went by and shows that the nanoparticles movement (dancing) slowed down and finally reached static status. Figure 1(c) shows the real time changes of catalytic activity and calorimetry as a function of temperature with set oxygen to methane ratio and nano-reactor pressure. For simplicity, only CO_2 was presented here. The catalyst activation and oscillation starting temperature and related structure and morphology information are revealed by correlating data in Figure (b) and (c). Further variations of CH_4 to O_2 ratio and temperature will change the periods and amplitudes accordingly.

For NiAu nanoparticles, we firstly investigated three extreme situations, i.e. reduction condition without vapor (H_2 & He), reduction condition with highest humidity vapor (H_2, H_2O & He) and only vapor at highest humidity level (H_2O & He), as shown in Figure 2. The particle retained in a structure of Ni core and Au shell in H_2 & He. Loose NiO structure formed outside the particle upon introduction of high humidity vapor (H_2, H_2O & He), and then condensed upon disappearance of H_2 in the inlet gas (H_2O & He).Then we varies humidity level from 0 to ~50% with H_2 and without H_2. We found an interesting oscillative transition between loose and condensed NiO layer formation, whose periodicity influenced by humidity level.

More experimental details and their interpretations will be presented on-site.

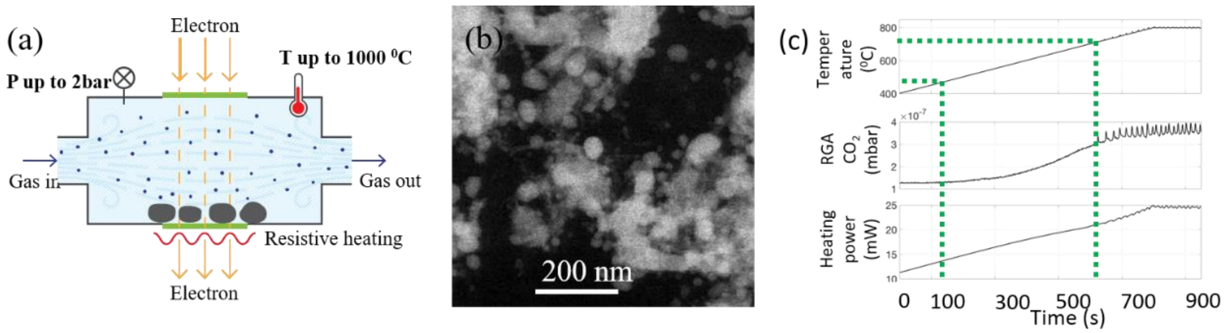

Figure 1. (a) Schematic view of the cross section of a Climate Nano-Reactor and its functionalities. (b) An HAADF image of Pd nanoparticles from the time-series image stack. (c) Catalytic behavior as a function of temperature continuous change from 400 to 800 ^{0}C.The RGA detected reaction product CO_2 increases obviously from around 420 ^{0}C and oscillates from about 700 ^{0}C; The heating power increases with temperature and oscillates with temperature oscillation to maintain required temperature.

References:

[1] Hansen, T.W., Wagner, *J.B.*, Controlled Atmosphere Transmission Electron Microscopy: Principles and Practice, Springer, 2016.
[2] Perez-Garza, H., *et.al.*, The “Climate” system: Nano-Reactor for in-situ analysis of solid-gas interactions inside the TEM, *IEEE-NEMS* (2016).
[3] Vendelbo, S.B., et al., Visualization of oscillatory behaviour of Pt nanoparticles catalysing CO oxidation. Nature Materials, 2014. **13**(9): p. 884-890.

https://doi.org/10.1017/S1431927622008200 Published online by Cambridge University Press