

High-Pressure Cell for *in situ* X-ray absorption study of nanocatalysts

Sophie Carenco,¹ Carlos Escudero,¹ Anders Tuxen,¹
Mahati Chintapalli,¹ Elzbieta Pach,¹ Mark West,² Jinghua
Guo,² Miquel Salmeron¹

¹Material Sciences Division, Lawrence Berkeley National
Laboratory, 1 Cyclotron Rd, Berkeley, CA 94720 (USA)

²Advanced Light Source, Lawrence Berkeley National
Laboratory (USA)

Nanocatalysts are used in a variety of electrochemical devices including fuel cells, lithium-air batteries and photochemical devices, as well as for gas-storage applications. In particular, the fine structure of the nanocatalysts (size and shape of nanoparticles, composition and gradients of composition, surfactants, interaction with the support, etc.) is critical for their performance and long-term stability.

Developing an intimate understanding of elementary processes such as molecular gas physisorption and chemisorption is a key step for designing the next generation of nanocatalysts. Moreover, the interaction of gas mixtures with the catalysts surface and the further processes of reaction and deactivation have to be deciphered.

In this purpose, our group developed a new gas cell for synchrotron-based *in situ* study of nanocatalysts by X-ray absorption (XAS).[1] Most prior XAS studies used hard x-rays and were bulk-sensitive, thus not best-suited for surface reactivity studies. Here, we used a soft X-ray source (Advanced Light Source, beamline 7.0.1) and a surface-sensitive detection method. This setup allowed us to access simultaneously the L or M edges of the metal nanoparticle catalysts and the K edges of the molecular adsorbates (carbon, oxygen, etc.), providing a unique combination of informations, in an *in situ* fashion and in temperature and pressure conditions that are close to the industrial ones.[2]

The gas cell that we designed consisted of a small reactor volume of ca 1 mL that contained the nanoparticle catalysts and was operated under up to 1 bar of a well-controlled gas mixture flow. The high-pressure reactor body was separated from the ultra-high vacuum environment of the beamline by an ultra-thin X-ray transparent silicon nitride window. In situ heating was provided from the backside of the reactor by a 10 W infrared laser. This heating device provided fast and precise temperature control in the range 25-400°C and, contrary to traditional resistive heaters, it avoided any electrical noise in the measurement. X-ray absorption spectra were collected using the total electron yield method and were thus sensitive to the very surface of the nanocatalysts (2 nm).

Using this newly designed gas cell, we demonstrated *in situ* monitoring of carbon monoxide adsorption on cobalt foil and size-controlled cobalt nanoparticles. Deactivation of the catalysts due to surface oxidation was observed within minutes when using a pure CO feed. This was a result of partial CO dissociation on the metallic surface. On the opposite, the surfaces of the foil and of the size-controlled nanoparticles were shown to remain metallic when using a mixed CO/H₂ feed. Size-

effect of the nanoparticles on the kinetics of these various processes was then studied. It shown that, below 15 nm diameter, the particles size affects the ability of the surface to dissociate carbon monoxide molecules.

This model study demonstrated the potential of soft X-ray *in situ* gas cell for monitoring chemical reactions and deactivation processes on cobalt nanocatalysts. Extension to other classes of chemical and photochemical reactions is underway in our laboratories.

References

- [1] C. Escudero, M. Salmeron, *Surface Science* **2013**, *607*, 2.
- [2] C. Escudero, P. Jiang, E. Pach, F. Borondics, M.W. West, A. Tuxen, M. Chintapalli, S. Carenco, J. Guo, M. Salmeron, *Journal of Synchrotron Radiation* **2013**, *20*, 504.