

# HETEROGENEOUS CATALYSIS IN LIQUID PHASE; CHALLENGES ON FUNDAMENTALS AND ENGINEERING

Barbara L. Mojet, K. Seshan and Leon Lefferts\*  
Catalytic Processes and Materials, MESA+ and IMPACT,  
University of Twente, Enschede, Netherlands  
\*[l.lefferts@utw.utwente.nl](mailto:l.lefferts@utw.utwente.nl)

## Introduction

The catalysis community has been improving the level of understanding of heterogeneous catalysis based on the combination of kinetic information, both at steady state and in transient experiments, catalyst characterization and mechanistic studies. Model-catalyst studies, theory, detailed knowledge about the structure of catalysts studied with numerous characterization techniques, including *in-situ* studies, all contributed significantly. In many cases, catalysts have been developed and improved based on and inspired by the detailed information thus obtained. This is certainly the case for catalysts operating in gas phase, despite the serious challenge caused by the “pressure-gap” between model catalyst studies and practical catalysis. In liquid phase however, the “pressure-gap” is better defined as a “density-gap”, referring to an enormous difference in density of the reaction phase between practical liquid-phase catalysis *versus* the requirement of low pressures in many characterization techniques. As a result, insight into the interaction of molecules in solution with catalyst surfaces is generally not available.

On the other hand, mass transfer limitations often compromise fundamental studies as well as performance in practical applications in liquid phase, because of relatively sluggish diffusion and because in most cases one of the reactants is a dissolved gas (e.g. H<sub>2</sub> or O<sub>2</sub>) at low concentration. This phenomenon causes concentration gradients inside catalyst particles, worsening catalyst performance in terms of activity and, in many cases and most importantly, selectivity. In addition, it is not commonly recognized, that concentration gradients are also not acceptable in *in-situ* catalyst characterization studies because the concentrations of reactants at every active site needs to be identical in order to observe correlations between concentrations and properties and surface-concentrations of adsorbed species. In other words, concentration gradients would corrupt data of *in-situ* studies in liquid phase.

This lecture offers a birds view of recent results in this field obtained in our lab, obtained with Attenuated Total Reflection Fourier Transform Infra-Red spectroscopy (ATR-IR) [1,2] and transiently operated reactors in liquid-phase [3] on the one hand, and on the other hand from the development of new, highly porous catalyst supports preventing concentration gradients [4].

## Materials and Methods

ATR-IR studies were performed for nitrite hydrogenation and CO oxidation on Pd and Pt catalysts in aqueous phase. Very thin catalyst layers on the internal reflection element in a home-built reactor were used in order to prevent concentration gradients, without affecting the mechanical stability of the thin layer. Nitrite/H<sub>2</sub> and CO/O<sub>2</sub> combinations were also used for transient experiments in aqueous phase, using a home built liquid phase pulse reactor with MS detection, equipped with two types of interfaces (based on membranes and electron-spray-ionization, respectively) to bridge the canyon between water and vacuum. Highly porous thin

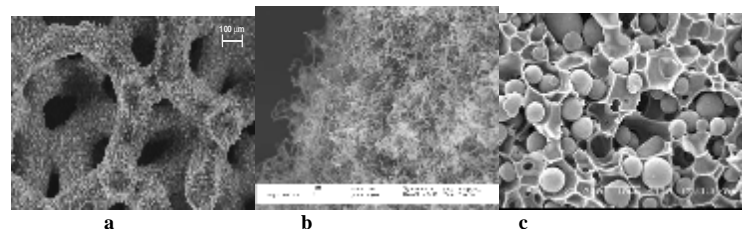
layers of carbon-nano-fibers (CNFs) were prepared by catalytic-chemical-vapor-deposition on e.g. Ni foams, which were used for transient experiments. Also, very small catalyst particles could be operated in fixed bed for transient experiments, by preventing unacceptable pressure drop.

## Results and Discussion

Highly porous thin layers on CNFs were prepared on Ni foams (Fig. 1a,b) on which Pt was deposited for transient experiments. Short diffusion pathways were achieved by using catalyst supported on silica particles as small as 5 micron; the pressure drop of the fixed bed was still acceptable by using extreme mono-disperse particles and by immobilizing the particles in the reactor space in a macro-porous polymer.

These catalyst supports enabled titration experiments with aqueous solutions of O<sub>2</sub>, H<sub>2</sub> and nitrite, as well as multi-product detection when pulsing a glucose solution over an oxygen covered Pt catalyst. Interestingly, transient responses revealed that H<sub>2</sub> significantly interacts with H-covered Pt, whereas O<sub>2</sub> does not interact at all with an oxidized Pt surface.

New insight was obtained from *in-situ* ATR-IR spectroscopy revealing that the rate determining steps in hydrogenation of nitrite on Pt and Pd are clearly different and this conclusion is supported by both steady state as well as transient experiments.



**Figure 1.** SEM micrographs of CNFs on Ni foams (a and b) and small Pt/SiO<sub>2</sub> particles immobilized in a polymer membrane.

## Significance

This work demonstrates how transient reactors and ATR-IR spectroscopy can be used to study the interaction of catalyst surfaces with molecules and ions in water, despite the presence of water. An important condition is to ensure that the catalyst is sufficiently accessible by introducing high porosity and/or short diffusion length and a few practical options are demonstrated.

## References

1. T. Bürgi, A. Baiker, *Adv. Catal.* 50, 227 (2006).
2. Sune D. Ebbesen, Barbara L. Mojet, Leon Lefferts, *Journal of Catalysis* 256, 15–23(2008).
3. D. Radivojević, M. Ruitenbeek, K. Seshan, L. Lefferts, *Journal of Catalysis* 257, 244–254 and 255–261 (2008).
4. J. K. Chinthaginjala, D. B. Thakur, K. Seshan and L. Lefferts, *Carbon* 46, 1638–1647(2008).