

# Time-Resolved and Operando XAS Studies on Heterogeneous Catalysts – From the Gas Phase Towards Reactions in Supercritical Fluids

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**Abstract.** X-ray absorption spectroscopy is a well-suited technique to uncover the structure of heterogeneous catalysts under reaction conditions. Different aspects of *in situ* cell design suitable for dynamic and catalytic studies are discussed. In addition, criteria are presented that allow estimating the influence external and internal mass transfer. Starting with studies on gas-solid reactions, including structure-activity relationships, this concept is extended to liquid-solid reactions, reactions at high pressure and in supercritical fluids. The following examples are discussed in more detail: partial oxidation of methane over Pt-Rh/Al<sub>2</sub>O<sub>3</sub>, reduction of a Cu/ZnO catalyst, alcohol oxidation over Bi-promoted Pd/Al<sub>2</sub>O<sub>3</sub> in liquid phase and over Pd/Al<sub>2</sub>O<sub>3</sub> in supercritical CO<sub>2</sub>, and batch reactions (e.g. CO<sub>2</sub>-fixation over zinc-based catalysts).

**Keywords:** in situ EXAFS, XANES, heterogeneous catalysis, supercritical fluids, spatially resolved spectroscopy

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## INTRODUCTION

Catalyst characterization during preparation, activation and under reaction conditions is important for a targeted catalyst development. X-ray absorption spectroscopy is a valuable tool for this, since it is element-specific, information both on amorphous and crystalline materials can be gained, and it can be used under reaction conditions [1-3]. To mimic the conditions of a catalyst under reaction conditions, the *in situ* cell should operate under conditions as closely as possible to that of a real catalytic reactor. First, this concept is discussed with respect to gas-solid reactions. Criteria are presented that allow assessing optimal conditions during time-resolved and *operando* XAS-studies. However, many reactions are performed in liquids, at elevated pressure or even in supercritical fluids where *in situ* studies are rarer but equally important [4]. Thus in the second part, the concept to derive structure-activity relationships is extended to those reactions.

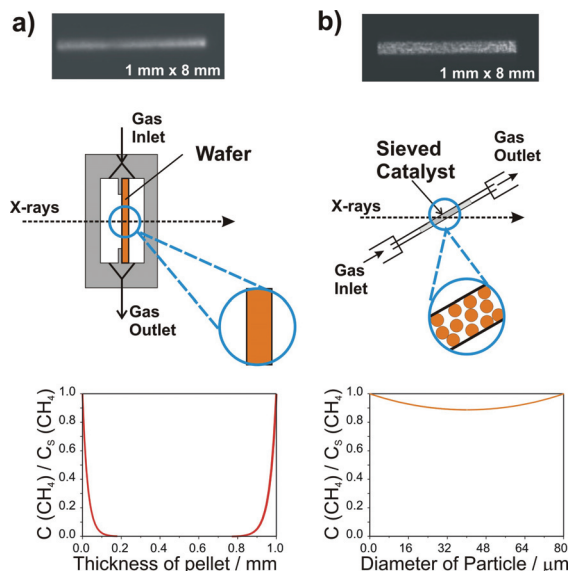
## IN SITU STUDIES ON GAS-SOLID REACTIONS

Already at normal pressure, *in situ* cells that provide *both* catalytic *and* structural information are a challenging issue. The main reason for this is that an *in*

*situ* cell is always a *compromise* between the spectroscopic demands (homogeneity of the sample, the energy of the X-ray absorption edge of the element of interest, transmission/fluorescence, size of the beam, intensity etc.), the catalysis (dynamic changes, nature of the fluid phase, reaction rate etc.) and the handling (ease of build up, robustness). Therefore a number of different *in situ* cells have been presented in literature, including some recent new developments (cf. [1,2,5] and references therein).

## Cell Design and Consequences for Time-Resolved and Operando XAS Studies

Figure 1 shows schematically two extreme cases for *in situ* cells presently applied. They will be used to underline the different aspects and to discuss the different criteria that lead to the best “compromise” for studying a catalyst *in situ*. A number of *in situ* cells exist that are intermediate between these two schematic designs. From spectroscopic point of view a catalyst pressed as a wafer (pellet) in a certain gas atmosphere and preferentially measured at low temperature is the optimal choice as indicated in the left part of Figure 1. However, if dynamic changes will be followed by *in situ* XAS or a catalytic reaction is studied, a design that is similar to a plug flow reactor and that contains a sieved fraction of the catalyst will be advantageous (right part of Figure 1).

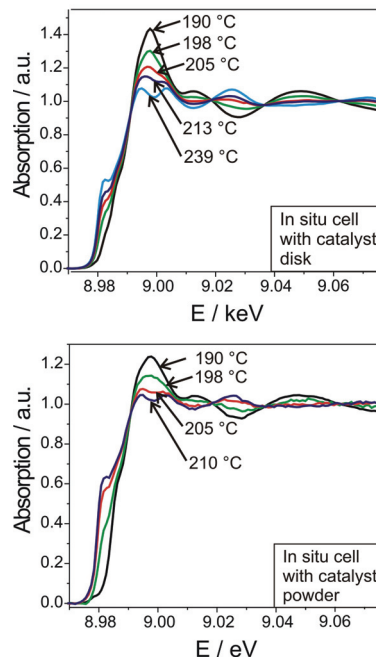


**FIGURE 1.** Two schematic *in situ* cells often used in literature (a) catalyst wafer in a reaction chamber and (b) sieved catalyst fraction in a plug flow-type reactor; top: transmission image as recorded by an X-ray eye; bottom: the calculated profile of the methane concentration in relation to the one on the surface during the total oxidation of methane.

To underscore this statement, the dynamic changes observed during the reduction of CuO/ZnO (diluted and pressed with BN) with the two cell designs (Figure 1) are depicted in Figure 2. Obviously, a different reduction behaviour is observed. The reduction of the Cu/ZnO-wafer is slower than the reduction of the CuO/ZnO-catalyst used as sieved fraction. Hence, not the chemical reaction but mass transfer of the reactants/products is rate-limiting. Recent calculations[5] showed that the internal mass transfer, which can be described by the effective diffusion coefficient  $D_e$  in the bulk material is rate-limiting. For round-shaped particles the reaction time  $\tau$  can be calculated according to the formula:

$$\tau_{\text{internal}} \cong \frac{\rho_{\text{CuO}} \cdot R_p^2}{6D_e \cdot c_{\text{H}_2}} \quad (1)$$

with the size of the particles  $R_p$ . For an effective diffusion coefficient of  $10^{-6} - 10^{-8} \text{ m}^2/\text{s}$ ,  $\tau$  amounts to 20 ms to 2 s. This has important consequences for time resolved studies in heterogeneously catalyzed reactions: Both the QEXAFS and the DEXAFS technique allow monitoring of structural changes in the millisecond regime[6,7]. Considering the reduction of the CuO/ZnO catalyst and equation (1), we can conclude that a reaction faster than  $\approx 1 \text{ ms}$  may be hampered by internal diffusion or even external mass transport, even in the ideal case of a sieved catalyst.



**FIGURE 2.** XANES data recorded during the reduction of 33wt%CuO/ZnO in 5% $\text{H}_2$ /He at a ramp rate of 2 K/min (two cases shown in Figure 1).

Also under stationary reaction conditions, internal mass transport properties may play a role. This is particularly true for fast reactions, such as the oxidation of methane. In heterogeneously catalyzed reactions, this is typically reflected by the “effectiveness factor” of the catalyst[8]. Due to the fact that the reactant (e.g. methane) is already consumed while it diffuses into the porous solid catalyst, the inner part of the catalyst may not contribute to the same extent to the reaction as the outer part of the catalyst pellet. In extreme cases, the concentration of one of the reactants drops to less than 1% and thus the inner part will not contribute to the reaction at all. Due to the fact that EXAFS experiments typically probe the whole catalyst, this will also strongly affect the spectroscopic result. Figure 1 (bottom) shows as an example the methane concentration gradient during the total oxidation of methane, calculated on the basis of a reaction rate constant  $k_r = 1.55 \cdot 10^3 \text{ s}^{-1}$  for methane oxidation and an effective diffusion coefficient  $D_e = 1.1 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$  (cf. refs. [5,9]). Whereas the concentration in an 80  $\mu\text{m}$  large particle only drops to 90% of the surface concentration, the concentration of methane in the self-supporting disk drops to less than 10% already at a penetration depth of 70  $\mu\text{m}$ . Considering the net thickness of 1 mm, transmission XAS studies will only to a *minor* extent monitor the part of the catalyst, where the reaction occurs. In addition, the effectiveness is with 3% much lower for the wafer than for a particle of 80  $\mu\text{m}$  (88% effectiveness). The concentration gradient depends on

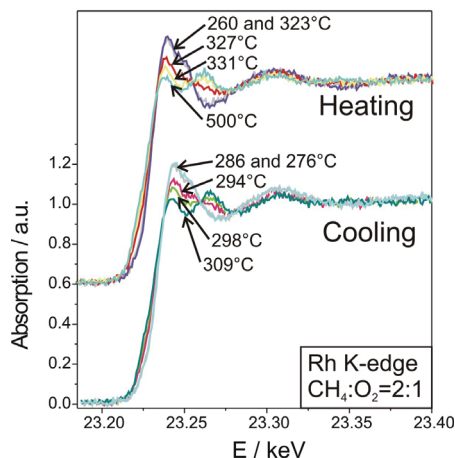
both, the reaction rate (rate constant  $k_r$ ) and the effective diffusion coefficient  $D_e$  (cf. ref. [5,8]).. For a

$$\psi = L_c \sqrt{\frac{k_r}{D_e}} \leq 3 \quad (2)$$

the concentration drops to less than 10% to the center of the catalyst particle ( $L_c$  characteristic length defined as half of the thickness for a disk and 1/6 of the particle diameter for round-shaped particles, cf. ref. [8]). Hence, this criterion is well-suited to estimate the influence of internal mass transport limitations during *in situ* spectroscopic studies.

### Partial Oxidation of Methane over 2.5%Pt-2.5%Rh/Al<sub>2</sub>O<sub>3</sub>

Extracting both catalytic and structural properties of a catalyst under reaction conditions is nowadays considered an important prerequisite to establish structure-performance relationships of catalysts [2,3,5]. This is particularly important, if the catalyst changes upon cooling from the reaction temperature and/or upon air exposure. The partial oxidation of methane over 2.5%Pt-2.5%Rh/Al<sub>2</sub>O<sub>3</sub> is a well-suited example for this since the catalyst structure changes significantly under reaction conditions. A powdered catalyst (sieve fraction 100  $\mu$ m) was used and both catalytic activity and structure were determined simultaneously.



**FIGURE 3.** Rh K-edge XANES data during partial oxidation of methane over 2.5%Rh-2.5%Pt/Al<sub>2</sub>O<sub>3</sub> while heating and cooling down in the reaction mixture.

The catalyst was prepared by flame-spray pyrolysis [10] using Pt(II)acetylacetonate, Rh(II)acetylacetonate together with aluminium sec-butoxide in xylene. Both platinum and rhodium were in oxidized state according to XANES- and EXAFS analysis. Catalysts, that were subject to EXAFS/XANES analysis after partial methane oxidation at 500 °C showed hardly any changes. In contrast to a pure Rh/Al<sub>2</sub>O<sub>3</sub> catalyst

prepared by a different procedure [11], both Rh and Pt were in oxidized state. Only slight changes in the EXAFS analysis were found after reaction, e.g. partly metallic contributions. However, when performing the studies *in situ* during heating up in a reaction mixture of methane/oxygen (ratio 2:1) both the Rh- and the Pt-constituent were reduced (Figure 3). The reduction occurred exactly at the temperature where the reaction ignited. The same effect was found during cooling: The partial oxidation to hydrogen and CO stopped at the temperature where the metallic species disappeared and the Rh and Pt-components reoxidized. This shows on the one hand the importance of the *in situ* studies in this example, on the other hand the study demonstrates that metallic-like Rh and Pt-species are the active sites in the reaction. Probably, metallic-like sites are better suited to activate methane than fully oxidized metallic clusters. Further studies were recently performed on different noble metal supported catalysts to gain deeper insight into the reaction mechanism.

## TOWARDS REACTIONS IN LIQUIDS AND AT ELEVATED PRESSURE

Many industrially relevant reactions, particularly in fine chemistry, are performed in liquid phase, often even at elevated pressure. Two different types can be distinguished: continuous-flow and discontinuous reactions in stirred tanks or autoclaves. In the field of high pressure reactions, catalysis performed in supercritical media or under conditions close to supercritical conditions of the solvent have recently attracted particular interest [4,12]. However, only a few *in situ* studies have been reported in liquid phase and at elevated pressure. Therefore first EXAFS/XANES studies on reactions in conventional liquids at normal pressure and then reactions at higher pressure, in particular in supercritical fluids, are discussed here.

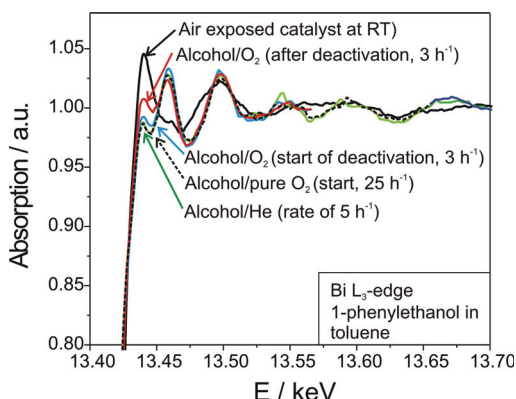
### *In Situ* Cells for Liquid Phase Reactions and at Elevated Pressure

Similarly as in gas-phase reactions external and internal mass transfer needs to be considered during dynamic changes (e.g. temperature, gas atmosphere) or during reaction. During the reduction of a 5%Pd/Al<sub>2</sub>O<sub>3</sub> by benzyl alcohol in toluene we e.g. observed that the reduction of palladium occurred at 80 °C within less than 5 min using PdO/Al<sub>2</sub>O<sub>3</sub> as powder, whereas the reduction over the same catalyst pressed as wafer took more than 45 min[5]. The effects of the internal mass transfer need to be treated in a similar way as in gas-phase but, particularly, due to the lower mass transfer coefficient of the reactants in the liquid phase compared to the gas phase, external mass transfer

often also plays a significant role [5]. Therefore small particles are required both during dynamic studies and if structure-performance relationships are targeted.

### Structure-Activity Relationships in Liquid Phase Alcohol Oxidation over Pd-Bi/Al<sub>2</sub>O<sub>3</sub>

Alcohol oxidation is an important reaction in fine chemistry and there is still a controversial debate in literature whether oxidized or reduced noble metal species are the active species in alcohol oxidation [13,14]. For this purpose, 0.75%Bi - 5%Pd/Al<sub>2</sub>O<sub>3</sub> was investigated during the oxidation of 1-phenylethanol to acetophenone. Both the Pd K- and the Bi L<sub>3</sub>-edge XAS spectra were taken and Figure 4 shows the changes that were observed under the different reaction conditions for bismuth. Further, the reaction rate is included. Under reaction conditions when directly changing from alcohol/He/toluene to alcohol/O<sub>2</sub>/toluene, bismuth is in reduced state and the catalytic activity is highest. Using pure oxygen for a longer time leads to oxidation of the bismuth promoter and a deactivation. This deactivation of the catalyst is in agreement with separate lab reactor experiments [13] where it was also concluded that at too high oxygen concentrations in the solvent a deactivation occurred.



**FIGURE 4.** Bi L<sub>3</sub>-edge XANES data during selective oxidation of 1-phenylethanol over 5%Pd-0.75%Bi/Al<sub>2</sub>O<sub>3</sub>; the reaction rate is given in brackets.

Corresponding changes to the Bi oxidation state were found at the Pd K-edge [13]. However, the variations were much smaller, probably, since the Pd-particles are only oxidized on the surface (Bi was selectively deposited on top of the particles, which makes EXAFS surface sensitive [13]). These results evidence that metallic Pd-species are the active species in the reaction and give indirect information on the Bi promoter. Furthermore the studies show that, similar to gas-solid reactions, structure-performance relationships can also be established in liquid phase that can give important insight into the active sites and the structure of the catalyst.

### Benzyl and Cinnamyl Alcohol Oxidation in Supercritical Carbon Dioxide

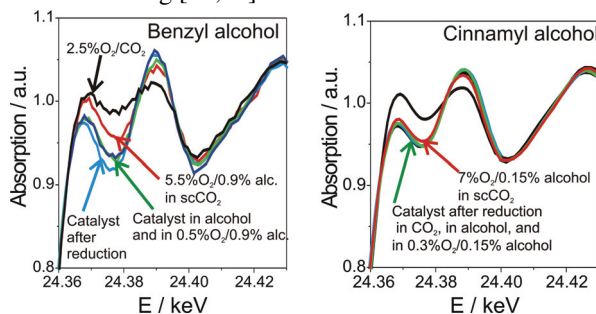
The use of supercritical fluids (SCFs) has been found beneficial in a number of reactions for different reasons [4,12]. SCFs allow combining liquid-like properties such as density or high solvation power and gas-like properties. Moreover, they show favourable mass transport properties. Nevertheless, understanding of heterogeneously catalyzed reactions in these media is still in its infancy and has only recently gained growing attention using *in situ* spectroscopy. One recently studied example is the oxidation of benzyl and cinnamyl alcohol in scCO<sub>2</sub>. The reaction rate of benzyl alcohol oxidation is > 10 times higher in scCO<sub>2</sub> than in toluene. However, at high oxygen concentrations (> 6 mol% O<sub>2</sub> in a mixture of 0.9% alcohol/CO<sub>2</sub>) it drops, which is not observed for cinnamyl alcohol.

Also in this case it can be speculated that Pd is surface oxidized during the selective oxidation of benzyl alcohol when the oxygen concentration is increased, similarly as in the case of 1-phenyl-ethanol oxidation over 0.75%Bi - 5%Pd/Al<sub>2</sub>O<sub>3</sub>. However, imitating the experiment in liquid phase fails for different reasons: (a) the reaction rate is much lower, (b) alcohol and oxygen mass transfer are different, (c) the solubility of oxygen in conventional solvents is much lower. In fact, performing the reaction in toluene with benzyl alcohol and oxygen leads even in the presence of pure oxygen not to a deactivation of the catalyst. Also no structural changes are observed under these conditions by EXAFS.

Therefore special efforts were made to build up a continuous-flow cell, which allows simultaneous monitoring of the structure by XANES/EXAFS and of the catalytic activity. Due to the fact that near the critical point small changes in pressure strongly affect the density of the reaction mixture, special efforts were put into pressure stabilization [15]. In order to minimize internal and external mass transfer, a sieved fraction of a shell-impregnated catalyst was used. The Pd-concentration was limited to 0.5%, to guarantee a sufficient dispersion of the catalyst that is required since the oxidation/reduction is only expected on the surface of the Pd-particles. Results in the XANES region for both the selective oxidation of benzyl alcohol and cinnamyl alcohol are depicted in Figure 5. As expected the Pd/Al<sub>2</sub>O<sub>3</sub> catalysts is reduced after alcohol exposure, and re-oxidized in oxygen/scCO<sub>2</sub>. Whereas the catalyst used for the selective oxidation of benzyl alcohol was also re-oxidized at a high oxygen concentration in the presence of the alcohol (which led to a deactivation of the catalyst), this was not observed for cinnamyl alcohol. The latter seems to be more reducing under the conditions applied and



therefore does not show any deactivation due to surface oxidation of the Pd-particles. These XANES results are also supported by corresponding EXAFS data and fitting [15,16].



**FIGURE 5.** XANES spectra at the Pd K-edge taken after pre-reduction of a 0.5%Pd/Al<sub>2</sub>O<sub>3</sub> catalyst during selective oxidation of benzyl alcohol and cinnamyl alcohol; the catalytic activity decreased in case of benzyl alcohol oxidation at higher oxygen concentration while it remained unchanged in case of cinnamyl alcohol oxidation.

### *In situ* Studies in Batch Reactors

Many of the reactions in liquid phase and at elevated pressure are performed in stirred tank reactors or autoclaves. Also preparation of catalysts (e.g. deposition precipitation, impregnation, etc.) is typically performed in such reactors. This requires also *in situ* studies in those cases. Therefore we recently designed an autoclave cell that contains two pairs of Be-windows which allows monitoring of both the solid and the liquid phase by XAS at two positions. This allowed elucidating the structure of Zn-based catalysts during the formation of propylene carbonate from propylene oxide in scCO<sub>2</sub>, the Ru-catalysed formylation of amines and the synthesis of Mo and W oxide nanorods under hydrothermal conditions [17].

### CONCLUSIONS AND OUTLOOK

Structure-performance relationships on heterogeneous catalysts can give important insight into the active site and the mechanism of the respective catalytic reaction. Preferentially, both catalytic performance (activity, selectivity) and structure are measured simultaneously. This goal and also the study of dynamic changes of the catalyst structure require the design of appropriate *in situ* cells – suitable criteria were discussed. In the different examples, it was demonstrated how the concept can be extended from gas-solid to liquid-solid and even reactions at elevated pressure and in supercritical fluids. Particularly, in the field of liquid phase and at elevated pressure only a few studies are known until now. Important further fields are the structural identification of catalyst promoters and catalyst poisons. Recently, it was also observed

that strong gradients in temperature and gas composition may have a strong effect on the catalyst structure in a catalytic reactor, requiring spatially resolved X-ray absorption spectroscopy under *in situ* conditions [18]. Finally, for a targeted catalyst development, studies during preparation and activation of catalysts are required as well.

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