Electronic Supporting Information

Role of powders and coatings for relating catalytic activity and structure of Pt in emission control catalysis

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1 X-ray Absorption Spectroscopy: Linear combination analysis

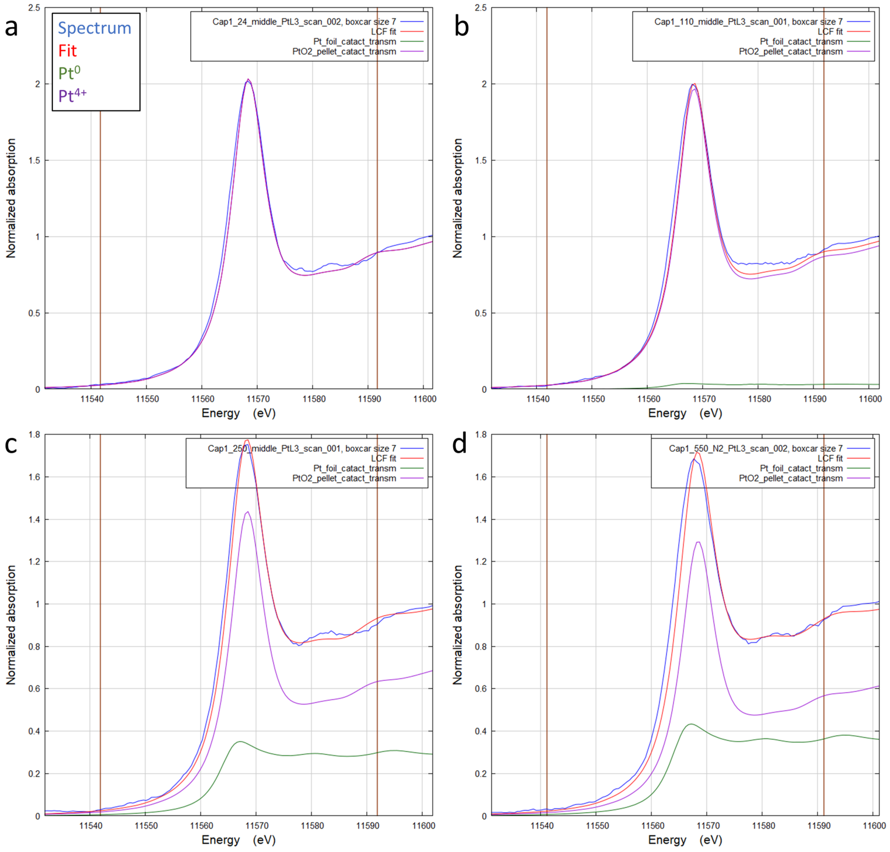

Fig. 1 LCA of the XANES spectra at the Pt L_3-edge of the powder packed bed at the middle position. The smoothed data, the fit and the contributions of Pt^0 (Pt foil) and Pt^{4+} (PtO_2) to the fit. The vertical lines in the figures display the energy range used for the fits. The spectra are displayed in blue, the LCA results in red, the contribution of Pt^0 in green and the contribution of Pt^{4+} in purple. a) 24 °C, b) 87 °C, c) 193 °C, d) 375 °C

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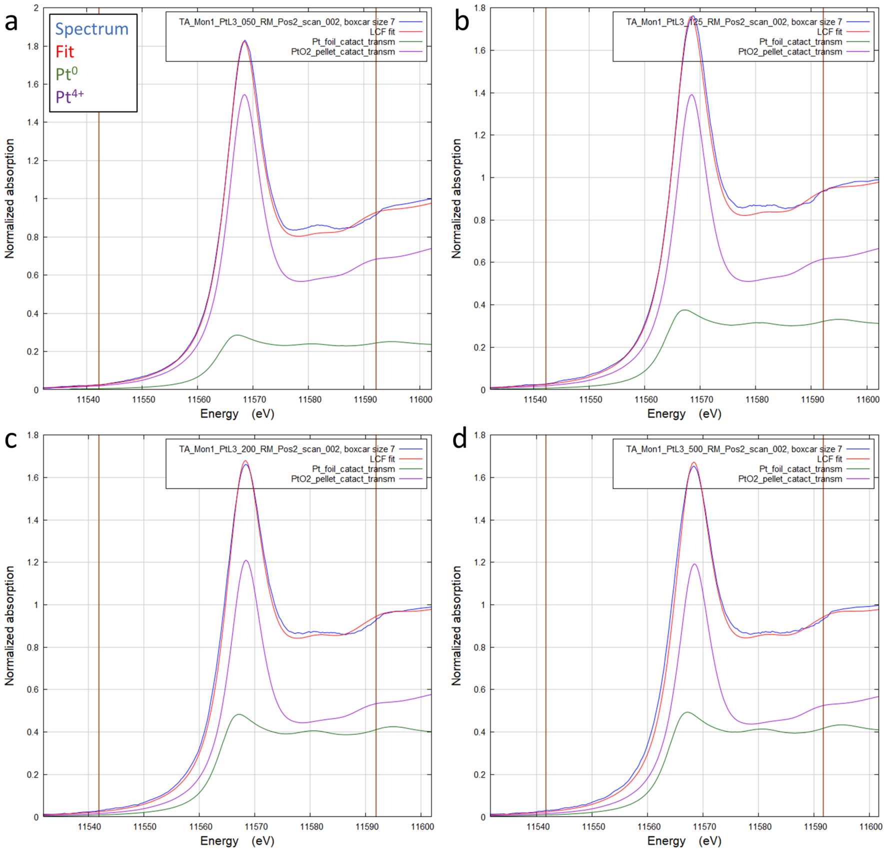

Fig. 2 LCA of the XANES spectra at the Pt L$_3$-edge of the coated monolith wall at the middle position. The smoothed data, the fit and the contributions of Pt^0 (Pt foil) and Pt^{4+} (PtO$_2$) to the fit. The vertical lines in the figures display the energy range used for the fits. The spectra are displayed in blue, the LCA results in red, the contribution of Pt^0 in green and the contribution of Pt^{4+} in purple. a) 25 °C, b) 108 °C, c) 172 °C, d) 500 °C

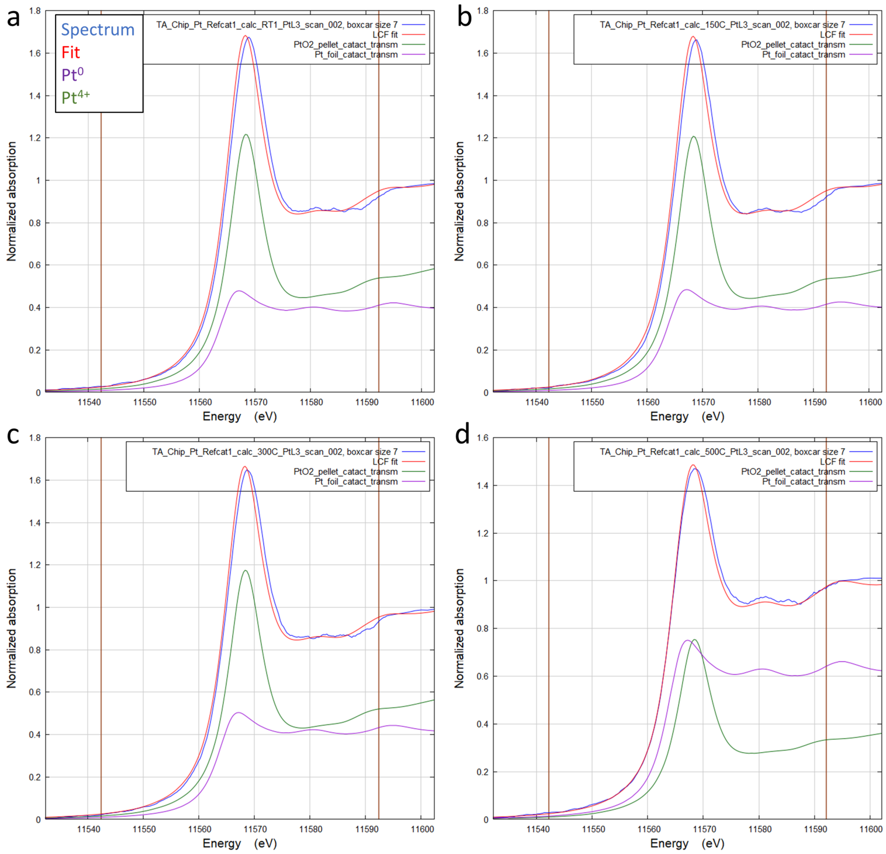

Fig. 3 LCA of the XANES spectra at the Pt L_3-edge of the coated chip at the central position. The smoothed data, the fit and the contributions of Pt^0 (Pt foil) and Pt^{4+} (PtO_2) to the fit. The vertical lines in the figures display the energy range used for the fits. The spectra are displayed in blue, the LCA results in red, the contribution of Pt^0 in purple and the contribution of Pt^{4+} in green. a) 22 °C, b) 136 °C, c) 272 °C, d) 451 °C

2 Support contribution to the catalytic activity

γ-Al_2O_3 did not show any significant CO conversion below 400°C for a gas flow of 50 $\frac{ml}{min}$ containing 1000 ppm CO and 10% O_2 in He and Ar. The powder bed used for this experiment consisted of 5.8 mg of pure γ-Al_2O_3 with a sieve fraction of 100 - 200 μm. The 1.9 wt.% Pt/γ-Al_2O_3 catalyst from Fig. 1 d was tested under almost identical conditions and showed full CO conversion already at 165 °C. Therefore, the 1.9 wt.% of Pt are much more active for CO oxidation than the γ-Al_2O_3 support.

3 Normalized CO conversion rates calculation

The CO conversion rates normalized to the amount of Pt from the spatially resolved gas phase experiments were calculated in the following way:

$$\frac{dx_{CO}}{dt\ m_{Pt}} = \frac{conversion}{length} \cdot \frac{dV_{CO}}{dt} \cdot \frac{1}{\frac{m_{Pt}}{length}} \cdot \frac{\rho_{CO}}{m_{mol,\ CO}}$$

Hereby, the first term $\frac{conversion}{length}$ multiplied by the second term $\frac{dV_{CO}}{dt}$ provides the information, how much CO is being converted per time and catalyst length in $\frac{ml}{mm\ min}$. By dividing with $\frac{m_{Pt}}{length}$, the information of how much CO is being converted per time and amount of Pt is obtained in $\frac{ml}{mg\ min}$. Multiplying by the density of CO converts the volume of CO into a mass of CO. When this mass of CO is divided by the molar mass of CO, the amount of CO molecules is obtained. This results in a unit of $\frac{mol\ of\ CO}{mg\ of\ Pt\ \cdot\ minute}$. For these calculations, the conversion per length of catalyst are obtained from the spatially resolved conversion measurements. To be precise, it was obtained from the first half of the catalysts respectively, since the gradients were constant in this area. The mass of Pt per length was calculated by dividing the amount of Pt the catalyst contained by the total length of the catalyst. The volume flow of CO was 50 $\frac{ml}{min}$ $\cdot$ $1000 ppm$. The density of CO is 1.14 $\frac{Kg}{m^3}$

and the molar mass of CO is 28.01 $\frac{g}{mol}$.

4 Coating thickness estimation

The washcoat thickness h was estimated by the respective washcoat mass in combination with the catalysts density and the coated area.

$$h = \frac{m}{\rho\ A} \tag{1}$$

Hereby, m was the mass of the catalyst, A the coated area and ρ the density of the catalyst. The catalyst density ρ was assumed to be that of the support material γ-Al_2O_3 (Puralox TH 100/150, Sasol Germany GmbH) which exhibits a loose bulk density of 400 $\frac{g}{l}$. The following table displays the parameters of the coating process and the estimated average washcoat thicknesses.

	Coated area	Catalyst mass	Washcoat thickness
Coated chip	0.00451 dm^2	0.01264 g	701 μm
Coated monolith (1 wall)	4.355 dm^2	0.36 g	21 μm
Coated monolith (9 channel)	4.355 dm^2	1.536 g	88 μm

Table 1 Coated areas, catalyst masses and the resulting washcoat thicknesses of the washcoated samples.

5 Pressure drop calculations

The pressure drop (ΔP_b) per catalyst bed length (L_b) for the packed powder beds were estimated using the Ergun equation (cf. ref[1]):

$$\frac{\Delta P_b}{L_b} = \frac{150\mu_g(1-\varepsilon)^2 u}{d_p^2\varepsilon^2} + \frac{1.75\rho_g(1-\varepsilon)u^2}{d_p\varepsilon^2}$$

The voidage ε was assumed to be 0.6, which is a typical value for pouring of spherical particles. The gas density ρ_g was assumed to be that of air at 0°C, scaled by a factor of $\frac{273.15\ K}{T}$, with the temperature (T) in Kelvin, in order to account for the temperature dependent changes in density. The gas velocity u was calculated from the dosed gas flow scaled by a factor of $\frac{T}{273.15\ K}$ with T in Kelvin and divided by the reactor cross section. The characteristic length d_p was assumed to be the average of the sieve fraction, which is 150 μm. μ_g is the dynamic viscosity, assumed to be that of air due to the similar gas composition to air. It is calculated *via*[2,3]:

$$\mu = \frac{1.458 \cdot 10^{-6}\ T^{1.5}}{T + 110.4} \tag{2}$$

with T being the temperature in Kelvin. According to literature[4], the pressure drop along the catalyst bed should not exceed 20% of the total pressure. For our experiments, the pressure drop over the length of the catalyst bed was in the range of several mbar, which is below 1% of the total pressure and therefore well within the recommended limit.

6 Calculation of the Reynolds number

The Reynolds number[5] is defined by $Re = \frac{\rho_g u l_c}{\mu}$ with the gas density ρ_g, the flow speed u, the characteristic length l_c and the dynamic viscosity μ. All parameters apart from l_c have already been addressed in the previous section. This characteristic length is now referred to as $l_{c,ext}$ in order to distinguish between characteristic lengths l_c relevant for the outer gas transport and gas transport within pores of the catalyst. The following table displays what has been defined as internal and external characteristic lengths.

Note, that for the packed beds, the Reynolds number was adjusted by the multiplication with a factor $\frac{1}{1-\varepsilon}$. This factor accounts for the volume, blocked by the spherical particles with a typical voidage ε of 0.6. The critical Reynolds number, above which the flow profile changes from laminar into turbulent is 2300 for gas flows through reactors (e.g. packed bed, monolith) and $5 \cdot 10^5$ for overflown objects (e.g. coated chip, coated monolith wall). All calculated values are far below these critical Reynolds numbers, suggesting a laminar gas flow profile for all experiments.

	$l_{c,\text{ext}}$		$l_{c,\text{int}}$	
Packed beds	average sieve fraction	0.15 mm	volume to surface ratio of particles	25 μm
Coated chip	length of the coating	11 mm	washcoat thickness	701 μm
Coated monolith (1 wall)	length of the coating	7.5 mm	washcoat thickness	21 μm
Coated monolith (9 channel)	channel height	1 mm	washcoat thickness	88 μm

Table 2 Internal and external characteristic lengths for the different catalyst shapes.

7 Diffusion coefficient and efficient diffusion coefficient

In order to calculate mass transfer limitations, the diffusion coefficient $D_{CO,m}$ of carbon monoxide (CO) in the dosed gas mixture m is needed. Furthermore, $D_{CO,e}$ which is the effective (e) diffusion coefficient $D_{CO,e}$ of CO is also necessary.
The diffusion coefficient of a component k in a mixture m can be calculated *via*:

7.1 Diffusion coefficient

$$D_{k,m} = \frac{1-x_k}{\sum_{i=1;i\neq k}^{N} \frac{x_i}{D_{k,i}}} \tag{3}$$

For the applied gas mixture of CO, O_2 and N_2, this equation becomes:

$$D_{k,m} = \frac{1-x_{CO}}{\frac{x_{N2}}{D_{CO,N2}} + \frac{x_{O2}}{D_{CO,O2}}} \tag{4}$$

The diffusion coefficient $D_{k,m}$ of the component k, which is carbon monoxide in this case, in a mixture m depends on the concentrations x of CO, O_2 and N_2 as well as on the binary diffusion coefficients $D_{k,i}$ which are $D_{CO,N2}$ and $D_{CO,O2}$. These can be calculated *via*[5]:

$$D_{k,i} = \frac{18.583 \cdot T^{\frac{3}{2}} \cdot \sqrt{\frac{M_k+M_i}{M_k \cdot M_i}}}{p \cdot \sigma_{k,i}^2 \cdot \Omega} \tag{5}$$

Hereby, p is the pressure, T the temperature, M_i are the molar mass, $\sigma_{k,i}$ the molecules potential diameter within the Lennard-Jones Potential and Ω is the collision integral. A fit from displayed data within[5] lead to the following collision integral for $2.5 < \frac{k_B T}{\varepsilon_{1,2}} < 10$: $\Omega = -0.008 \cdot (\frac{k_B T}{\varepsilon_{1,2}})^3 + 0.0203 \cdot (\frac{k_B T}{\varepsilon_{1,2}})^2 - 0.178 \cdot (\frac{k_B T}{\varepsilon_{1,2}}) + 1.326$. Hereby, k_B is the Boltzmann constant and T the temperature. The $\varepsilon_{k,i}$ are force constants and $\varepsilon_{1,2} = \varepsilon_{CO,N2} = \sqrt{\varepsilon_{CO} \cdot \varepsilon_{N2}}$. The calculation of the CO diffusion coefficient for the gas mixture of 0.1 % CO, 10 % O_2 and 89.9 % N_2 resulted in the following equation:

$$D_{CO} = 8 \cdot 10^{-11} T^2 + 8 \cdot 10^{-8} T - 1 \cdot 10^{-5} \tag{6}$$

For this equation, the temperature is in units of K and the CO diffusion coefficient in units of $\frac{m^2}{s}$. The calculated CO diffusion coefficient was $3.07 \cdot 10^{-5}\ \frac{m^2}{s}$ at 99 °C and $3.68 \cdot 10^{-5}\ \frac{m^2}{s}$ at 150 °C. These two temperatures of 99 °C and 150 °C were those, at which mass transfer limitations were calculated.

7.2 Effective diffusion coefficient

$D_{i,e}$ is the effective diffusion coefficient. In order to estimate this coefficient, the respective pore diameter regime has to be taken into account. The Pt/Al_2O_3 catalyst consisted mostly of commercial γ-Al_2O_3 (Puralox TH 100/150 from the company Sasol). This commercial support material exhibits a pore diameter of 22 nm which places the diffusion into the 'Knudsen diffusion' regime according to literature[5]. In this regime, the effective diffusion coefficient can be calculated *via* $D_{k,eff,i} = \frac{\varepsilon_p\ d_p}{3\ \tau_k} \cdot \sqrt{\frac{8\ R\ T}{\pi\ M_i}}$ with the index k standing for Knudsen, eff standing for effective and i being the gas of interest (i = CO in this case). T is the temperature in Kelvin, R is the ideal gas constant ($8.314462 \cdot 10^7\ \frac{erg}{K\ mol}$), d_p is the pore diameter which is 22 nm and τ_k is the tortuosity (typically between 3 and 4 according to literature[5]). For this estimation τ_k was assumed to be 3.5 ± 0.5. The molar mass of CO is $M_{CO} = 28.01\ \frac{g}{mol}$. The porosity ε_p can be estimated by the ratio of the pore volume to the catalyst volume. The commercial support exhibits, according to the company a pore volume to mass ratio of $0.8\ \frac{ml}{g} \leq \frac{V_p}{m} \leq 1.1\ \frac{ml}{g}$. Therefore ε_p can be calculated to be $\frac{V_p}{V_p + V_{Al2O3}} = \frac{\frac{V_p}{m} \cdot m}{\frac{V_p}{m} \cdot m + \frac{m}{\rho_{Al2O3}}} = \frac{\frac{V_p}{m}}{\frac{V_p}{m} + \frac{1}{\rho_{Al2O3}}} = \frac{(0.95 \pm 0.15)\frac{ml}{g}}{(0.95 \pm 0.15)\frac{ml}{g} + \frac{ml}{3.94\ g}} = 0.78 \pm 0.03$.

Hereby the error is calculated *via* $\Delta\frac{V_p}{m} \cdot \frac{d\varepsilon_p}{d\frac{V_p}{m}} = \Delta\frac{V_p}{m} \cdot (\frac{1}{\frac{V_p}{m} + \frac{1}{\rho_{Al2O3}}} - \frac{\frac{V_p}{m}}{(\frac{V_p}{m} + \frac{1}{\rho_{Al2O3}})^2}) = 0.15\ \frac{ml}{g} \cdot (\frac{1}{0.95\ \frac{ml}{g} + \frac{ml}{3.94\ g}} - \frac{0.95\ \frac{ml}{g}}{(0.95\ \frac{ml}{g} + \frac{ml}{3.94\ g})^2}) = 0.03$

The error can be estimated *via* error propagation: $D_{k,eff,i} \pm \Delta D_{k,eff,i} = D_{k,eff,i} \pm (|\frac{dD_{k,eff,i}}{d\varepsilon_p} \cdot \Delta\varepsilon_p| + |\frac{dD_{k,eff,i}}{d\tau_k} \cdot \Delta\tau_k|) = \frac{\varepsilon_p\ d_p}{3\ \tau_k} \cdot \sqrt{\frac{8\ R\ T}{\pi\ M_i}} \pm (\Delta\varepsilon_p + \frac{\varepsilon_p\ \Delta\tau}{\tau}) \cdot \frac{d_p}{3\tau_k}\sqrt{\frac{8\ R\ T}{\pi\ M_i}} = 0.0004546\frac{cm^2}{s\ K} \cdot \sqrt{T} \pm 0.0000801\frac{cm^2}{s\ K} \cdot \sqrt{T}$

The calculated effective CO diffusion coefficient was $8.94 \cdot 10^{-7}\ \frac{m^2}{s}$ at 99 °C and $9.39 \cdot 10^{-7}\ \frac{m^2}{s}$ at 150 °C.

8 Obtaining the reaction rate constant

In order to estimate the Damköhler number II (Da_{II}) for external mass transfer limitations and the Thiele modulus (Φ) for internal mass transfer limitations, the reaction rate constant k is needed. In this chapter, the method of obtaining this parameter is displayed. For lean CO oxidation on Pt/Al_2O_3 it is possible to calculate the reaction rate. In order to calculate Da_{II} and Φ, one has to be sure, that the calculated value for the reaction rate k is not affected by external and internal mass transfer limitations. The following procedure ensured, that the observed reaction rate constant k_{obs} was indeed identical to the real reaction rate constant k:

1) Choosing the right system and temperature: For the X-ray absorption spectroscopy experiments and the spatially resolved gas phase investigation experiments, the packed powder beds were chosen. These exhibit the lowest chance for external mass transfer limitations and they are the only ones, for which the Weisz modulus (valid only for spherical particles) can be estimated.

2) Choosing the right temperature: The temperature, at which k is calculated has to be in the kinetic regime (between 5% and 20% CO conversion) in order to lower the chance of mass transfer limitations. Here 150 °C (XAS experiments) and 99 °C (Spatially gas phase experiments) were chosen.

3) Calculate the observed reaction rate constant k_{obs} and use it for calculating the Mears criterion for external mass transfer limitations, since it depends on the observed, and not on the real reaction rate constant. Check, if the system was subject to external mass transfer limitations.

4) Calculate the Weisz modulus and check if the Weisz-Prater criterion for internal mass transfer limitations is fulfilled.

5) If external and internal mass transfer limitations can be excluded, then the observed reaction rate constant k_{obs} at this temperature is identical to the real reaction rate constant k. If this is the case, $k_{obs,\ packed\ powder\ bed} = k$. Then k can be used to estimate Da_{II} and Φ at that temperature for all catalytic systems.

8.1 Observed reaction rate constant

The reaction rate constant for this reaction originates from the equation $\frac{1}{\gamma}\ \frac{dc_c}{dt} = k \cdot c_A^{r_a} \cdot c_B^{r_b}$ for the reaction $\alpha\, A + \beta\, B \rightarrow \gamma\, C$. Here A is the concentration of CO, B that of O_2 and C that of CO_2. α, β and γ are the stoichiometry factors and c_c is the concentration of component C, which is CO_2. Since the reaction order r_{O2} is 0 and the reaction order of CO $r_{CO} = 1$,

the equation can be simplified. Here, we substitute the change in CO_2 by the change in CO under the assumption that each CO molecule ends up in CO_2. This leads to the equation: $k = \frac{dc_{CO}}{C_{CO}\ dt}$. The change of the CO concentration over time can be expressed by the total change of the CO concentration over the residence time $\tau_{residence}$. The residence time $\tau_{residence}$ is hereby $\tau_{residence} = \frac{\varepsilon \cdot V_{powder}}{\dot{V}_{Troom} \cdot \frac{T}{T_{room}}}$. Here, the cylindrical reactor volume, in which the powder resides is multiplied by the voidage ε of 0.6 and is then divided by the total gas flow, which is scaled by the ratio of the temperature and the room temperature at which the gas flow (50 $\frac{ml}{min}$) was dosed. This was necessary to account for the temperature dependent gas expansion. This temperature scaling approach originates from the ideal gas law. With the knowledge that the gas concentration changes over the timespan of the the residence time, $k = \frac{dc_{CO}}{C_{CO}\ dt}$ can be rewritten as $k = \frac{X_{CO}}{\tau_{residence}}$. The CO conversion X_{CO}, which is the change in CO concentration divided by the total CO concentration is hereby a dimensionless number between 0 and 1 (e.g. a CO conversion of 0.07 means that 7 % of the CO were converted during the time τ it took the gas to flow through the catalyst).
For the packed powder beds, the observed reaction rate constants were: $k_{obs}(99\ °C) = 1.14\ \frac{1}{s}$ and $k_{obs}(150\ °C) = 12.5\ \frac{1}{s}$.

8.2 Mears criterion

With the Mears criterion[6], the presence external mass transfer limitations can be estimated.

$$\frac{R\ r_p^2}{c_{i,0}\ D_{i,e}} < \frac{1}{n} \tag{7}$$

Hereby, n is the reaction order, r_p is the sieve fraction, c_{in} the applied CO concentration which was 1000 ppm, $D_{i,e}$ the effective diffusion coefficient and $R = \frac{X_{CO}\ n\ c_{in}}{V\ \tau}$ the CO conversion rate per volume. Hereby, V is the volume of the catalyst bed and τ is the residence time. The residence time can be calculated *via*: $\tau = \frac{V_{packed\ bed}}{\dot{V}}$, with the volume flow $\dot{V} = \dot{V}_{dosed}\ \frac{T}{273.15\ K}$. R can be rewritten *via* the ideal gas law: $R = \frac{X_{CO}\ p\ c_{in}}{R\ T\ \tau}$ with the gas constant R, the pressure p and the temperature T. When this expression is inserted into the Mears criterion, it becomes:

$$\frac{X_{CO}\ r_p^2}{\tau\ D_{CO,e}} < 1 \tag{8}$$

The calculated values for this criterium were 0.03 for the packed powder bed used for the spatially resolved gas phase measurements at 99 °C and 0.30 for the packed powder bed at 150 °C, used for the XAS investigations. Since both values are below 1, external mass transfer limitations are unlikely.

8.3 Weisz modulus

The Weisz modulus can be calculated *via*:

$$\Psi = \frac{L_{c,int}^2 \cdot (n+1) \cdot r \cdot \rho_k}{2 \cdot D_{i,e} \cdot c_{i,0}} \tag{9}$$

Hereby, $L_{c,int}$ is the internal characteristic length, n the reaction order, r the reaction rate of CO in respect to the amount of catalyst and ρ_k the catalysts density (assumed to be the loose bulk density of the utilized Al_2O_3 support material) of 400 $\frac{g}{l}$, $D_{i,e}$ the effective diffusion coefficient of i = CO. The reaction rate in respect to the amount of catalyst can be calculated *via* $r = \frac{\dot{n}_{Mol}}{m_{catalyst}} = \frac{\dot{V}_{CO}}{m_{catalyst}} \cdot \frac{\rho_{CO}}{m_{mol,CO}} = \frac{conv_{CO} \cdot 0.001 \cdot 0.000833 \frac{l}{s}}{m_{catalyst}} \cdot \frac{1.145 \frac{g}{l}}{28.01 \frac{g}{mol}} = \frac{X_{CO}}{m_{catalyst}} \cdot 3.40516 \cdot 10^{-8}\ \frac{mol}{s}$. $c_{i,0}$ is the concentration of the component i (i = CO in this case) at the beginning of the reaction (t = 0). The initial CO concentration was $c_{i,0} = 1000\ ppm \cdot \frac{\rho_{CO}}{m_{mol,CO}} = 0.001 \cdot \frac{1.145 \frac{g}{l}}{28.01 \frac{g}{mol}} = 4.08783 \cdot 10^{-5}\ \frac{mol}{l}$

The calculated values for this Ψ were 0.0002 for the packed powder bed used for the spatially resolved gas phase measurements at 99 °C and 0.0027 for the packed powder bed at 150 °C, used for the XAS investigations. The Weisz-Prater criterion states, that internal mass transfer limitations are unlikely to occur, if the Weisz modulus is below 1. Since this is the case for both powders at the chosen temperatures, internal mass transfer limitations are unlikely.

8.4 Reaction rate constant

Now that both packed powder beds have been investigated in terms of mass transfer limitations, it can be concluded, that the observed reaction rate constants can be assumed to be unaffected by mass transfer limitations. Therefore the obtained values were also utilized for calculating Da_{II} and Φ for all catalyst shapes:

X-ray absorption spectroscopy experiments: $k(150\ °C)\ \approx\ 12.5\ \frac{1}{s}$

Spatially resolved gas phase experiments: $k(99\ °C)\ \approx\ 1.14\ \frac{1}{s}$

9 External Mass transfer limitations

The Damköhler number II Da_{II} indicates if the catalyst is subject to external mass transfer limitations. Its calculation is based on the following literature[5,7,8]:

$$Da_{II} = \frac{k \cdot c_0^{n-1}}{k_g \cdot a} \tag{10}$$

Hereby, k is the reaction rate constant, k_g is the global mass transport coefficient, a is the interfacial area, c_0 the initial concentration and n the reaction order. Since lean CO oxidation in case of a non-pre reduced catalyst, which is not CO poisoned (as revealed by our XAS results) exhibits a reaction order of $n = 1$, the equation can be simplified to $Da_{II} = \frac{k}{k_g \cdot a}$. The expression $k_g \cdot a$ can generally be rewritten as the mass transfer coefficient β, times the inverse characteristic length $\frac{1}{l_{c,ext}}$. This results in the equation:

$$Da_{II} = \frac{k \cdot l_{c,ext}}{\beta} \tag{11}$$

The mass transfer coefficient β can be calculated *via* $\beta = \frac{Sh \cdot D_{CO}}{l_{c,ext}}$. Hereby, D_{CO} is the CO diffusion coefficient and Sh is the Sherwood number. Within the framework of the analogy of heat and mass transfer, the Sherwood number Sh for mass transfer can be set equal to the Nusselt number Nu for heat transfer. Within the Nu number, the Prandtl number Pr has to be replaced by the Schmid number Sc. Finally Da$_{II}$ can be written as:

$$Da_{II} = \frac{k \cdot l_{c,ext}^2}{Nu \cdot D_{CO}} \tag{12}$$

All parameters except of the Nusselt number Nu have been discussed in the previous chapters. Within the book[7], different expressions are provided for Nu for different systems. For the monolith, which is much longer than the channel diameter, the Nusselt number is approximately $Nu \approx 3.66$. For the overflown plate (the chip and the monolith wall), it is $Nu = 0.664 \cdot \sqrt{Re} \cdot Pr^{\frac{1}{3}}$ and for the packed powder bed it is $Nu = 2 + 0.6 \cdot \sqrt{Re} \cdot Pr^{\frac{1}{3}}$. These expressions include one novel parameter, which is the Prandtl number Pr. For the packed powder bed, the Prandtl number Pr can be replaced by the Schmidt number Sc, which is $Pr = Sc = \frac{\nu}{D_{CO}}$. For the overflown plates (chip and monolith wall), it is $Pr = \frac{\nu \rho c_p}{\lambda}$. ρ is hereby the density, λ is the thermal conductivity and c_p the specific heat conductivity. These parameters were also assumed to be for air due to the high similarity of air to the dosed gas composition.

10 Internal Mass transfer limitations

The Thiele modulus Φ is used for determining, if a catalyst is subject to internal mass transfer limitations. It is calculated *via*:

$$\Phi \;=\; l_{c,int}\,\sqrt{\frac{k\;c_s^{n-1}}{D_{k,eff,i}}} \tag{13}$$

Here, $l_{c,int}$ is the internal characteristic length, k is the reaction rate constant, c_s is the surface concentration, n is the reaction order and D_e the effective diffusion coefficient. Due to $n = 1$, the surface concentration vanishes and the equation becomes:

$$\Phi \;=\; l_{c,int}\,\sqrt{\frac{k}{D_{k,eff,i}}} \tag{14}$$

All of the parameters within this equation have been discussed in the previous sections. The error of the Thiele modulus calculation can be determined by error progression *via* $\Phi \pm \Delta\Phi = \Phi \pm (|\frac{d\Phi}{dL_c} \cdot \Delta L_c| + |\frac{d\Phi}{dD_{k,eff,i}} \cdot \Delta D_{k,eff,i}|) = \Phi \pm \Phi\,(\frac{\Delta L_c}{L_c} + \frac{\Delta D_{k,eff,i}}{2\;D_{k,eff,i}})$.

The effectiveness factor[9] for spherical pellets η_{int} can be calculated from the Thiele modulus *via* $\eta = \frac{3}{\Phi}\,(\frac{1}{tanh(\Phi)} - \frac{1}{\Phi})$. This formula was utilized for the packed powder beds. For washcoats, the effectiveness factor can be calculated *via* $\eta = \frac{tanh(\Phi)}{\Phi}$.

Values close to $\eta = 1$ indicate, that the catalyst is unlikely to suffer from internal mass transfer limitations, while values of less than 1 suggest the presence of internal mass transfer limitations.

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