sReactivation of CeO$_2$-based Catalysts in the HCl Oxidation Reaction: In situ Quantification of the Degree of Chlorination and Kinetic Modeling

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Deactivation of CeO$_2$-based catalysts in the HCl oxidation reaction proceeds via selective bulk chlorination of the active CeO$_2$ component to form CeCl$_n \times n$H$_2$O. We study the reactivation of two bulk-chlorinated CeO$_2$-based Deacon catalysts by oxygen treatment at 430 °C, namely pure CeO$_2$ and 20 mol% of CeO$_2$ supported on preformed ZrO$_2$ particles (20CeO$_2@$ZrO$_2$), with a dedicated experiment. In the flow reactor setup we determine in-situ the degree of chlorination of the catalyst by quantifying down-stream with in-situ UV-Vis spectroscopy the total amount of chlorine in the catalyst that is exchanged by reoxidation at 430 °C. The activity of deactivated 20CeO$_2@$ZrO$_2$ can be fully restored by oxygen exposure at 430 °C, while that of pure CeO$_2$ declines steadily. Since the UV-Vis analytics is fast and sensitive, we can follow the kinetics of reoxidation. To rationalize the observed kinetics, we develop a modified Johnson-Mehl-Avrami-Kolmogorov (JMAK) model based on a nucleation-and-growth approach for the reoxidation of the catalyst starting from the chlorinated phase. The fast reoxidation kinetics of chlorinated 20CeO$_2@$ZrO$_2$ is traced to a fast nucleation rate.

1. Introduction

Catalyst stability is a severe concern in heterogeneous catalysis and many ways of catalyst deactivation have been reported in literature, among which most studies have focused on sintering of the active component with the consequence of a reduction of the active surface area. However, there is a class of catalysts that undergoes chemical transformation under reaction conditions accompanied by a deterioration of catalytic performance. This kind of reaction-induced catalyst transformation is for instance encountered with the HCl oxidation reaction, the so-called Deacon process (Eq. (1)), which is employed to recover chlorine from the omnipresent byproduct HCl in many industrial processes:

$$4\text{HCl} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Cl}_2;$$

$$\Delta_h \text{H} = -114 \text{kJ/mol}$$

For the Deacon process, low stability of the catalyst has been an ongoing problem that had deferred its industrial commercialization by 130 years. For instance, the original catalyst CuO, invented by Deacon 1868, readily undergoes bulk chlorination towards CuCl$_2$. Since CuCl$_2$ is volatile at a reaction temperature above 400 °C, the catalyst is gradually lost during operation. Only in the year 2000 Sumitomo Chemical commercialized an active and stable Deacon catalyst based on RuO$_2$ that is supported on rutile TiO$_2$.

Already very early, the catalyzed HCl oxidation over oxide surface was envisioned to be composed of a reduction step by HCl followed by a reoxidation step of the chlorinated oxide by
molecular oxygen.\textsuperscript{[5]} For the commercialized RuO\textsubscript{2}/rutile-TiO\textsubscript{2} catalyst these reduction and oxidation steps are not bulk transformations of the catalysts, but rather take place at the surface only.\textsuperscript{[7]} However, for the case of CeO\textsubscript{2}-based catalysts, a promising and viable alternative to RuO\textsubscript{2}, it was recognized that they deactivate in the Deacon reaction through bulk chlorination,\textsuperscript{[8–12]} although being partly reactivated with excess oxygen in the reaction feed at reaction temperatures of typically 430 °C.\textsuperscript{[6,13,14]} Improved chemical stability against bulk chlorination is achieved by mixing CeO\textsubscript{2} with ZrO\textsubscript{2} either in the form of solid solutions\textsuperscript{[15,16]} or as CeO\textsubscript{2} deposited on preformed ZrO\textsubscript{2} particles.\textsuperscript{[17,18]} The degree of chlorination that is directly correlated to the deactivation of the catalyst can be quantified in-situ by prompt gamma activation analysis (PGAA)\textsuperscript{[13,19]} but also ex-situ either by thermogravimetric analysis (TGA-MS)\textsuperscript{[9]} or by quantitative X-ray diffraction (XRD: Rietveld refinement).\textsuperscript{[8,18]}

Here, we report a dedicated experiment for quantifying the degree of chlorination of the CeO\textsubscript{2}-based catalyst in the very same reactor with which also the catalytic Deacon tests are performed. With this unique experiment, we can readily follow in-situ the kinetics of its reaction via reoxidation. We exemplify this method as a proof-of-principle experiment with two Deacon powder catalysts, one pure CeO\textsubscript{2} and the other is 20 mol\% CeO\textsubscript{2} supported on preformed ZrO\textsubscript{2} particles (20CeO\textsubscript{2}@ZrO\textsubscript{2}). It turns out that the activity of pure CeO\textsubscript{2} is not fully recovered after reoxidation of the previously bulk-chlorinated sample. However, the activity of 20CeO\textsubscript{2}@ZrO\textsubscript{2} is quantitatively recovered after the second reactivation cycle. In addition, the reoxidation of 20CeO\textsubscript{2}@ZrO\textsubscript{2} is much faster compared to that of pure CeO\textsubscript{2}. In a phenomenological kinetic model based on a nucleation-and-growth approach, we can describe the faster reoxidation of the supported catalyst by a higher nucleation rate due to the support (ZrO\textsubscript{2}) surface.

**Experimental Section**

**Experimental Details**

The Deacon reaction was conducted in a custom fixed-bed flow reactor.\textsuperscript{[20]} The reactor comprises the gas supply, the quartz tube reactor, heated by a computer-controlled furnace, and UV/vis analytics (Ocean Optics USB4000 with a DH-2000-BAL light source) for chloride quantification. The following gases were used in the reaction measurements: HCl (99.995%), O\textsubscript{2} (99.999%) and Ar (99.999%) from AirLiquide, and the flow rate of gases was controlled by digital mass flow controllers (MKS Instruments 1179B). Prior to feeding the gas mixture into the reactor, Ar was dried using a water absorption cartridge (ALPHAGAZTM purifier H\textsubscript{2}O-free, AirLiquide). The absorbance at a wavelength of $\lambda_{\text{max}}$ = 329 nm (absorption maximum of chlorine) is proportional to the chlorine space time yield (STY) that is defined as the molar amount of product per time and mass catalyst.

Besides catalytic activity tests, the flow reactor with the UV-Vis analytics can be employed to quantify the degree of chlorination of the catalyst after Deacon reaction. In doing so we reoxidized the chlorinated catalysts by oxygen exposure and the replaced chlorine from the catalyst is quantified by UV-Vis spectroscopy. Since the sensitivity of the UV-Vis spectroscopy is high and the data acquisition is fast enough, this dechlorination process of the (partly) chlorinated catalyst can be followed in-situ as a function of time. Iodometry is employed to calibrate the extinction in the UV-Vis signal to absolute Cl\textsubscript{2} concentrations. The detailed calibration steps are shown in Section 1.3 of the Supporting Material.

The proposed method for quantifying the degree of catalyst chlorination is in situ. In particular, we developed a reliable measurement protocol that is summarized in Figure 1 with the total flow set to 15 cm\textsuperscript{3}STPmin\textsuperscript{−1} (sccm) and the catalyst kept at 430 °C. Each reaction step is followed by a purging step with pure Ar to remove the weakly held species from the reactor walls until the baseline of the chlorine UV-Vis signal is stable. The Deacon reaction experiments is first carried out under so-called “mild” condition with the reaction feed Ar:HCl:O\textsubscript{2} = 10.5:1:5.3. After the catalytic activity has reached steady state, the activity in terms of space time yield (STY) can be determined. Subsequently pure Ar is purged and the deactivation experiment is performed under so-called “harsh” condition with a feed ratio of Ar:HCl:O\textsubscript{2} = 9:4.5:1.5. When the catalyst is fully deactivated due to in-depth chlorination, pure Ar is purged. To quantify the degree of chlorination, the deactivated CeO\textsubscript{2}-based catalyst is exposed to 50 vol.% O\textsubscript{2} (balanced by argon) for 5 h at the reaction temperature until the deactivated catalyst is fully reoxidized. During reactivation, oxygen replaces chlorine in the catalyst, and the replaced chlorine can be quantified by UV-Vis spectroscopy. After completion of the reactivation step, the reactor is purged with Ar. This terminates the first deactivation/reactivation cycle. The deactivation/reactivation cycle is repeated twice in order to estimate the activity loss due to restoration.

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![Figure 1](image.png)  
*Figure 1. The measurement protocol (reaction feed composition) for determining the degree of chlorination of a CeO\textsubscript{2}-based catalyst after full deactivation. The total flow rate is always 15 sccm and the catalyst is kept at 430 °C. Steady state activity experiments are performed before and after restoration (reactivation).*

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Further details about catalyst preparation and the employed characterization methods can be found in the Section 1 of the Supporting Material.

Computational Details

During the reactivation step described in Experimental Details, we monitor the reoxidation kinetics through the evolution of Cl$_2$ as a function of time. We employ a phenomenological approach to model the differences between the reoxidation kinetics of the samples. We first note that the measured Cl$_2$ signal during reoxidation released by the reaction [Eq. (2)].

$$\text{CeCl}_3 + \text{O}_2 \rightarrow \text{CeO}_2 + \frac{3}{2}\text{Cl}_2$$

represents the derivative of the fraction of the transformed phase (CeO$_2$), denoted as $e$, over time, $t$: $x_e(t) = \frac{de}{dt}$, i.e., the rate of the phase transformation. The fraction of transformed phase as a function time $x(t)$ can therefore be obtained by the numerical integral of the Cl$_2$ signal over time. All our reoxidation signals (e.g., the blue area in Figure 2) have a characteristic shape where the initial rate of transformation is zero, goes through a maximum and then gradually returns to zero. The integral of the Cl$_2$ signal over time is a sigmoidal function. This behavior suggests a self-accelerating process, which is typical for a nucleation and growth mechanism. Since the phase transformation requires the formation of nuclei of the new phase, the initial growth rate is zero if no nuclei have been formed previously.

The kinetics of such a phase transition can be described using the Johnson-Mehl-Avrami-Kolmogorov (JMAK) approach. The JMAK theory assumes that nucleation occurs randomly at a constant rate per sample volume. Nucleation in the JMAK theory can proceed either spontaneously from an oversaturated (or undercooled) vapor or aided by solid surfaces. As the existence of a supersaturated vapor is highly unlikely in a flow reactor, we assume that available surfaces of catalyst support (SiO$_2$ and ZrO$_2$) and untransformed materials (CeO$_2$, CeCl$_3$) serve as heterogeneous nucleation sites for CeO$_2$ during reoxidation. However, we note that the JMAK theory cannot distinguish between nucleation mechanisms, and different nucleation mechanisms will only be reflected in different nucleation rates. The nuclei then grow at a constant rate until the whole sample volume is transformed. The transformed dimensionless volume fraction $e_B = \frac{V_B}{V_{tot}}$ of phase B (CeO$_2$) as a function of time can be expressed by the well-known Avrami equation [Eq. (3)].

$$e_B(t) = 1 - e^{-k_{eff}m^{1/2}}$$

where $k_{eff}$ is an effective rate constant and $m$ is the order of the growth process, with the integer values 1, 2, 3 corresponding to 1D, 2D and 3D growth.

As will be shown in Sections 3.1 and 3.2 our system does not fulfill some of the assumptions made in the derivation of the standard Avrami equation: (1) Our catalyst does not undergo a pure phase transition. Rather it is a phase transformation due to a chemical reaction of CeCl$_3$ with O$_2$. (2) The catalyst bed contains some untransformed oxide at the start of the reoxidation reaction, which means that the number of nuclei and the volume fraction of oxidized phase are not zero initially. (3) Our supported sample grows as a layer on top of ZrO$_2$, which contains approximately 25% of the supported CeO$_2$ in 20CeO$_2$@ZrO$_2$. The remaining 75% form CeO$_2$ particles. The sample therefore must expose two different growth modes, possibly with different rates. (4) The detected Cl$_2$ signal represents the derivative of the transformed volume fraction with respect to time, $\frac{de}{dt}$. Therefore, we derive a modified JMAK model in the supporting material that accounts for these additional features, whose derivation is shown in detail in Section 2 of the supporting information. Denoting $n_{nuc}$ as the number of nuclei, $r$ as the radius and $e_{GO}$ as the volume fraction of CeO$_2$, we finally arrive at three coupled differential equations [Eqs. (4)–(6)].
We conduct two cycles of deactivation/reactivation for pure CeO$_2$ catalyst under the HCl oxidation reaction at $T=430$ °C as summarized in Figure 2. Firstly, we measure the steady state activity of the CeO$_2$ catalyst under mild condition (Ar:HCL:O$_2$: 10.5:1.5:3) with the STY being 20 molCl$_2$ kg$_{cat}$ h$^{-1}$. After Ar purging, the catalyst is exposed to a harsh reaction mixture (Ar:HCL:O$_2$: 9:4.5:1.5). During 1.5 h on stream, the STY of CeO$_2$ declines continuously and saturates finally at a residual activity that is likely due to hydrated CeCl$_2$\cite{11,18}. In the next step, the deactivated CeO$_2$ catalyst is reactivated by the mixed atmosphere of O$_2$ and Ar (Ar:O$_2$:7.5:7.5). The broad chlorine peak is attributed to the chlorine signal that is formed by the oxidation of CeCl$_3$×nH$_2$O. This reactivation step takes about 1.4 h. With the assumed reaction of Equation (2), we can determine the chlorination degree, defined as $n$(CeCl$_3$)/(n(CeCl$_3$) + $n$(CeO$_2$)), of the deactivated CeO$_2$ sample: The integrated chlorine peak area is 6.7 molCl$_2$ kg$_{cat}$, combined with the catalyst amount of 26 mg and molar mass of 172.1 g/mol of CeO$_2$, that results in a chlorination degree of 75 ± 3 % for the fully-deactivated CeO$_2$ catalyst. Consistent with literature\cite{11,18}, CeO$_2$ is found to be not fully transformed to hydrated CeCl$_3$. Last, we measure again the steady state activity under mild reaction condition that turns out to be 16.4 molCl$_2$ kg$_{cat}$ h$^{-1}$ and is hence 17 % lower than that of the fresh one.

Subsequently, we repeat the deactivation/reactivation cycle. The pure CeO$_2$ catalyst under harsh reaction condition fully deactivates after 1.7 h on stream. The replaced chlorine amount of 6.3 molCl$_2$ kg$_{cat}$ translates to a chlorination degree of 68 ± 4%, which is slightly lower than after the first deactivation. The activity of the CeO$_2$ catalyst after the second reactivation is 15.4 molCl$_2$ kg$_{cat}$ h$^{-1}$, that is 6% lower than after the first and 23 % lower than the initial activity.

In summary, we observe that the deactivated CeO$_2$ catalyst can be restored by reoxidation with pure oxygen, but the steady state activity declines steadily after each restoration step. The decline in chlorination degree may be traced to the formation of larger CeO$_2$ particles as will be shown in the following section. In Figure 3, we summarize the same deactivation/reactivation series and evaluation procedure for the 20CeO$_2$@ZrO$_2$ catalyst. For the 20CeO$_2$@ZrO$_2$ sample 20 mol% CeO$_2$ is coated on preformed ZrO$_2$ particles, forming a covering ultrathin CeO$_2$ layer (5 mol% and 1.6 ± 0.2 nm thick) together with adhering CeO$_2$ particles (15 mol%).\cite{14} The activity of the fresh 20CeO$_2$@ZrO$_2$ catalyst under mild condition is 20.2 molCl$_2$ kg$_{cat}$ h$^{-1}$. When switching to harsh reaction conditions, the STY of 20CeO$_2$@ZrO$_2$ drops until it has saturated after 7 h on stream with a residual activity that is likely due to ZrO$_2$, and CeCl$_3$×nH$_2$O. Next, the deactivated 20CeO$_2$@ZrO$_2$ catalyst is fully recovered by exposure to O$_2$ at 430°C. In this reactivation step, the reoxidation of 20CeO$_2$@ZrO$_2$ is completed after 0.4 h and is hence substantially faster than the reoxidation of the pure CeO$_2$ catalyst. The integrated chlorine peak contains 2.3 molCl$_2$ kg$_{cat}$ h$^{-1}$. Combined with the amount (30.3 mg) and molar mass (132.8 g/mol) of 20CeO$_2$@ZrO$_2$ this implies a chlorination degree of 100 % for fully deactivated 20CeO$_2$@ZrO$_2$.

The activity of reactivated 20CeO$_2$@ZrO$_2$ under mild condition is 18.5 molCl$_2$ kg$_{cat}$ h$^{-1}$, 8% lower than that of the fresh
one. In the next deactivation/reactivation cycle, the chlorine peak area due to oxygen replacement contains 2 mol Cl₂ kg⁻¹ cat, leading to a chlorination degree of 91 ± 2%. We finally evaluate the activity of 20CeO₂@ZrO₂ after the second reactivation step to be 18.3 mol Cl₂ kg⁻¹ cat h⁻¹ which is practically identical to that of 20CeO₂@ZrO₂ catalyst after the first reactivation.

2.2. Characterization of the fresh, deactivated and reactivated CeO₂-based catalysts

The structures of the fresh, deactivated and reactivated CeO₂ and 20CeO₂@ZrO₂ catalysts were thoroughly characterized by XRD (Figure 4a). The observed reflections of the fresh CeO₂ sample belong to the cubic fluorite structure (ICDD NO. 00–034-0394). The CeCl₃·nH₂O reflections are detected for the deactivated CeO₂ sample, clearly evidencing bulk chlorination and thus explaining the rapid deactivation of the pure CeO₂ sample. As summarized in Table 2, Rietveld refinement of XRD data of deactivated CeO₂ sample shows that 76% of the pure CeO₂ sample is transformed to CeCl₃·7H₂O. This result agrees remarkably well with the fraction of hydrated CeCl₃ determined from UV-Vis quantification of the dechlorination peak, providing 77% of CeCl₃ for the pure CeO₂ sample. Interestingly, the crystallite size of CeO₂ in the deactivated CeO₂ sample (19 nm) is larger than the initial crystallite size (10 nm). Our interpretation of these results from Rietveld refinement is that small CeO₂ particles are completely transformed to CeCl₃·7H₂O upon...
chlorination. Only larger particles remain partly as CeO$_2$ after chlorination, thus increasing the average size of CeO$_2$ crystallites. The XRD pattern of reactivated CeO$_2$ is attributed to a cubic fluorite structure. The width of the reflections of the reactivated sample (Figure 4a: top, blue) has visibly decreased compared to the fresh sample (Figure 4a: top, black). Consistently, we obtain an average crystallite size of around 25 nm for the reactivated CeO$_2$ sample, substantially larger than the fresh one (10 nm; Table 1). This increase in particle size explains the observed activity loss of the reactivated CeO$_2$ sample.

The XRD pattern of the fresh 20CeO$_2$@ZrO$_2$ catalyst (Figure 4a: bottom) consists of a superposition of the cubic phase of CeO$_2$ (ICDD NO. 00-034-0394) and the monoclinic phase of ZrO$_2$ (ICDD NO. 00-036-0420). For the deactivated 20CeO$_2$@ZrO$_2$ sample, the CeCl$_3$×nH$_2$O concentration is determined to be 21 mol% in agreement with the nominal percentage of monoclinic phase of ZrO$_2$ with a crystallite size of CeO$_2$ of around 7.8 nm (Table 1), slightly increased with respect to the fresh sample (6.5 nm, Table 1).

In Figure 4b we summarize the corresponding Raman experiments of fresh, deactivated and reactivated CeO$_2$ and 20CeO$_2$@ZrO$_2$. The Raman spectrum of fresh CeO$_2$ is dominated by a strong band at 464 cm$^{-1}$ that corresponds to the $F_{2g}$ mode (Ce–O–Ce vibration) of the CeO$_2$ fluorite phase$^{[21,22]}$. The Raman spectrum of deactivated CeO$_2$ exhibits an additional feature at 119 cm$^{-1}$ that belongs to pure CeCl$_3$×nH$_2$O$^{[18]}$. Therefore, Raman spectroscopy evidences bulk chlorination in agreement with the XRD results in Figure 4a. The reactivated sample shows only a strong Raman band at 464 cm$^{-1}$, thus indicating a complete transformation to the CeO$_2$ fluorite structure.

The double feature at 470 cm$^{-1}$ of 20CeO$_2$@ZrO$_2$ indicates the coexistence of CeO$_2$ (fluorite structure) and ZrO$_2$ (monoclinic structure) (Figure 4b). The Raman spectrum of the deactivated 20CeO$_2$@ZrO$_2$ also exhibits an additional feature at 119 cm$^{-1}$, while the CeO$_2$-related contribution at 464 cm$^{-1}$ disappears. This is clear evidence that all the CeO$_2$ species have been transformed to hydrated CeCl$_3$ after harsh Deacon reaction. The Raman spectrum of the reactivated sample reveals a stronger ceria peak intensity than the fresh one, indicating that ceria particles have grown in size after the reactivation step fully consistent with XRD experiments in Figure 4a.

In Figure 4c, we compile X-ray photoemission (XP) spectra of fresh, deactivated and reactivated CeO$_2$ and 20CeO$_2$@ZrO$_2$. Compared to the fresh CeO$_2$ the XP spectrum of the deactivated CeO$_2$ shows the superposition of CeCl$_3$, CeO$_2$, and CeO$_2$ signals$^{[23,24]}$, suggesting that the CeO$_2$ has not been fully chlorinated under harsh Deacon condition, which is compatible with the Rietveld refinement of the XRD data. From XPS the chlorination degree turned out to be 64% (Table 2); the detailed fitting of XP spectra can be found in Figure S3. The XPS of reactivated CeO$_2$ is practically identical to that of the fresh sample that is indicative of a full recovery of the catalyst.

Fresh 20CeO$_2$@ZrO$_2$ exhibits a similar Ce 3d XP spectrum as the pure CeO$_2$, while that of the deactivated 20CeO$_2$@ZrO$_2$ catalyst comprises only features of CeCl$_3$×nH$_2$O consistent with the XRD quantification result. The Ce 3d spectrum of the reactivated sample is identical to the fresh one. However, the effective ceria concentration of the reactivated sample decreases from 53% to 41% (Table 2) which means that the ceria particles have partially agglomerated into larger adhering particles. Since XPS is surface-sensitive and the surface-to-volume ratio has decreased upon sintering, the Ce 3d signal intensity declines.

The TEM (Transmission electron microscopy) images and XEDS (X-ray energy dispersive spectroscopy) mappings of deactivated 20CeO$_2$@ZrO$_2$ in Figures 5a, b indicate a uniform distribution of Ce (blue) and Cl (yellow) across the ZrO$_2$ particles (green). Together with the low catalytic activity of hydrated CeCl$_3$ (cf. Figure 3) we conclude that the hydrated CeCl$_3$ is highly dispersed over the ZrO$_2$ particles after chlorination. The TEM images of the reactivated sample (Figures 5c, d) reveal that both the adhering thin CeO$_2$ layer and the CeO$_2$ particle on ZrO$_2$ particle structures have been recovered after oxygen treatment at 430°C. The TEM micrographs and the XEDS mappings look similar to those of the fresh sample (Figure S4), in accordance with the full recovery of the activity.

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**Table 1. Crystallite size and BET surface area of fresh, deactivated and reactivated CeO$_2$, 20CeO$_2$@ZrO$_2$ catalysts.** Catalytic activity of fresh and reactivated CeO$_2$, 20CeO$_2$@ZrO$_2$ catalysts. Chlorination degree of fresh, deactivated and reactivated CeO$_2$, 20CeO$_2$@ZrO$_2$ catalysts.

| Samples     | Crystallite Size [nm] | Surface area [m$^2$/g] | STY | CeO$_2$ | CeCl$_3$×nH$_2$O | ZrO$_2$ |
|-------------|----------------------|------------------------|-----|---------|------------------|---------|
| CeO$_2$     | n.a.                 | n.a.                   | 20.0 | 10.0    | 25%              | 76%     |
| Deactivated | 19 n.a.              | 46                     | 20.0 | 10.0    | 25%              | 76%     |
| Reactivated | 25 n.a.              | 26                     | 16.4 | 15.4    | 25%              | 76%     |
| 20CeO$_2$@ZrO$_2$ Deactivated | 6.5 n.a. | 12 | 16.4 | 15.4 | 25% | 76% |
| Reactivated | 7.8 n.a.             | 33                     | 18.5 | 18.5 | 25% | 76% |

[a] Determined by Rietveld refinement. [b] Determined by BET method. [c] Determined by fixed-bed flow reactor. [d] STY after first and second reaction.

**Table 2. The concentration of CeO$_2$, CeCl$_3$ of fresh, deactivated and reactivated CeO$_2$, 20CeO$_2$@ZrO$_2$ catalysts.**

| Samples     | CeO$_2$ content [mol%] | Chlorination degree [%] | Surface atomic concentration | Ce/ (Ce + Zr) | Cl/ (Ce + Zr) |
|-------------|------------------------|-------------------------|-------------------------------|---------------|---------------|
| CeO$_2$     | n.a.                   | 100%                    | 100%                          | 100%          | 100%          |
| Deactivated | 76%                    | 64%                     | 100%                          | 100%          | 100%          |
| Reactivated | n.a.                  | 100%                    | 100%                          | 100%          | 100%          |
| 20CeO$_2$@ZrO$_2$ Deactivated | 16.4 | n.a. | n.a. | 100% | 100% |
| Reactivated | 23 n.a.               | 41%                     | 100%                          | 100%          | 100%          |

[a] Determined by Rietveld refinement. [b] determined by XPS.
In order to demonstrate the high sensitivity of the present UV-Vis based reactor experiment we investigated the chlorination degree of stable CeO$_2$-based catalysts that have not suffered from bulk chlorination (cf. Figure 6). The integral chlorine intensities in the dechlorination peaks and the BET surface areas of CeO$_2$ and 20CeO$_2$@ZrO$_2$ are practically identical (cf. Figure 6). This observation points to a similar chemical nature of the active phases. The amount of chlorine accommodated at the surface of the CeO$_2$ particle can be determined from these experiments. It turns out that the chlorination degree of pure CeO$_2$ is about 10%, while that of 20CeO$_2$@ZrO$_2$ is 30%. The former value for pure CeO$_2$ agrees surprisingly well with the PGAA-derived value of about 10% reported in the literature.$^{[13]}$

For the case of pure CeO$_2$ with a BET surface area of maximum 46 ± 2 m$^2$/g (Table 1: fresh sample, BET surface decreases slightly upon Deacon reaction) and 30 mg catalyst, the total surface area is 1.38 m$^2$. From surface science experiments we know that the density of surface chlorine on CeO$_2$(111) is at least 1Cl atom/1.38 nm$^2$ but not more than 2Cl atoms/1.38 nm$^2$.$^{[25]}$ The upper limit is therefore 1.46 · 10$^{17}$ surface Cl atoms that corresponds to a maximum degree of chlorination of 0.8%. From this estimation we conclude that the found degree of chlorination of 10% corresponds to much more chlorine at CeO$_2$ than just realized by adsorbed chlorine on the surface.

2.3. Kinetics of the reoxidation process

We show experimentally that the fully and partially chlorinated CeO$_2$ and 20CeO$_2$@ZrO$_2$ catalysts can be reoxidized and therefore be reactivated by exposure to oxygen. We observe substantial differences between the studied catalysts regarding both the shape of the evolved chlorine signal, and the overall kinetics of the reoxidation process. The overall kinetics can be
described by the reaction half time $t_{1/2}$ at which half the material has reacted. For the pure CeO$_2$ sample we obtain a $t_{1/2}$ of 0.52 h and 0.55 h for the first and second reoxidation. For 20CeO$_2$@ZrO$_2$ we obtain 0.12 h for both reoxidation experiments. Moreover, we observe different shapes of the evolved chlorine signal during the reoxidation of the two samples. We employ the phenomenological model described in Experimental Section for the modelling of the experimental data.

For the reoxidation of the supported catalyst 20CeO$_2$@ZrO$_2$ we assume that most CeO$_2$ is formed in particle shape, and that the CeO$_2$ film supported on the ZrO$_2$ particles is negligible in a first approximation, since the reoxidation experiment measures the total Cl$_2$ evolved in the reoxidation of both the active film and the less active particle, and 75% of the CeO$_2$ assumes the form of particles in the fresh catalyst. However, we note that the highly dispersed CeO$_2$ film dominates the catalytic activity of 20CeO$_2$@ZrO$_2$ in the HCl oxidation. We further assume that the growth of the CeO$_2$ particles in the pure CeO$_2$ and 20CeO$_2$@ZrO$_2$ catalysts can be described by the same reaction order $m$ and rate constant for growth $k_{\text{grow}}$. However, we expect nucleation to be different in the two samples, using two different parameters $k_{\text{nuc,CeO}_2}$ and $k_{\text{nuc,CeO}_2@ZrO}_2$ that reflect the absence and presence of the ZrO$_2$ support. We therefore employ four parameters, $m$, $k_{\text{grow}}$, $k_{\text{nuc,CeO}_2}$ and $k_{\text{nuc,CeO}_2@ZrO}_2$, to model all four reoxidation experiments of the completely chlorinated samples (Figures 2, 3).

Since the supported catalyst is expected to exhibit two different growth modes (layer and particle), but our model only describes one growth mode (particle), we expect larger deviations for the supported catalyst. In order to avoid meaningless fit results, we assign the 20CeO$_2$@ZrO$_2$ catalyst a lower weight, which results in better fit of the CeO$_2$ reoxidation signal. The weights are 1 and 0.5 for the reoxidation of pure CeO$_2$ and 20CeO$_2$@ZrO$_2$.

While we employ the same reaction order and rate constants to describe the growth both in the pure and supported catalysts, we realize that the samples differ in several ways; for instance, the pure CeO$_2$ catalyst is not completely oxidized, which possibly influences the reoxidation kinetics.

Our model takes into consideration the state of the deactivated sample through the boundary conditions $r(0)$ (particle radius) and $\varepsilon_{\text{CeO}_2}(0)$ (volume fraction of residual CeO$_2$). The boundary conditions for $r(0)$ and $\varepsilon_{\text{CeO}_2}(0)$ for the pure CeO$_2$ catalyst are chosen based on the experimental result that only 75% of the sample has been chlorinated, that is, $\varepsilon_{\text{CeO}_2}(0) = 0.25$. The starting radius of the nuclei is taken from the Rietveld refinement (19 nm). The boundary conditions for the second reoxidation experiment are obtained in similar fashion as listed in Table 3. For the 20CeO$_2$@ZrO$_2$ catalyst, we observe that the first chlorination is complete, so both $\varepsilon_{\text{CeO}_2}(0)$ and $r(0)$ are zero. For the second reoxidation experiment, $\varepsilon_{\text{CeO}_2}(0) = 0.09$. We have no data on the residual CeO$_2$ particle radius, so that we chose $r(0) = 5$ nm, slightly smaller than the particle size after reoxidation (7.8 nm). We note that the model results are insensitive to the choice of the initial particle radius for $r(0) < 30$ nm due to the high growth rate obtained in the model fit.

### Table 3. Boundary conditions and weights for the kinetic model as obtained from experimental catalyst characterization.

| Sample    | Cycle | $\varepsilon_{\text{CeO}_2}(0)$ | $r(0)$ [nm] | $w$ |
|-----------|-------|---------------------------------|-------------|-----|
| CeO$_2$   | 1$^{st}$ | 0.24                           | 19          | 1   |
| CeO$_2$   | 2$^{nd}$ | 0.32                           | 19          | 1   |
| 20CeO$_2$@ZrO$_2$ | 1$^{st}$ | 0.32                           | 19          | 0.5 |
| 20CeO$_2$@ZrO$_2$ | 2$^{nd}$ | 0.09                           | 5           | 0.5 |

The parameters $m$, $k_{\text{grow}}$, $k_{\text{nuc,CeO}_2}$ and $k_{\text{nuc,CeO}_2@ZrO}_2$ are fitted by minimizing S through recursive parameter sweeping. The fitting results are given in Table 4. The fitted chlorine signals are displayed as a function of time in Figure 7. The agreement between model and experiment is quite good for both reoxidation cycles of pure CeO$_2$ (Figure 7a), as well as for the second reoxidation cycle of the supported catalyst (Figure 7b). For the first reoxidation cycle we observe a higher signal intensity, as well as a slow decay of the signal that our model is unable to reproduce. However, our model can describe the overall rate and reaction half time of the reoxidation reaction quite well, resulting in a faster reoxidation of the supported catalyst compared to the pure catalyst. Since our model assumes that the CeO$_2$ growth rate (50.9 nm (h bar)$^{-1}$) is unaffected by the presence of ZrO$_2$, the difference in the reoxidation kinetics is traced to a nucleation rate in the supported catalyst (192.9 (h nm bar)$^{-1}$) that is a factor of 32 higher than in the pure CeO$_2$ catalyst (5.89 (h nm$^2$ bar)$^{-1}$). While ZrO$_2$ itself is inert in the chlorination and reoxidation reaction, it can provide surface area where CeO$_2$ particles can nucleate, thereby accelerating the overall reoxidation reaction. Furthermore, we know from TEM imaging (Figure 5c, d) that the CeCl$_3$ particles are well-dispersed over the ZrO$_2$ surface, contributing to the high observed nucleation rate. While the overall nucleation rates seem similar, we emphasize that the resulting kinetics drastically differ for the two samples, which means that the experiment is highly sensitive to the nucleation rate. The high nucleation rate in the supported sample can be interpreted as the preference to form new CeO$_2$ particle presumably on the ZrO$_2$ surface over the growth of existing CeO$_2$ particles. This can possibly prevent the ripening of CeO$_2$ particles in successive reduction-oxidation cycles and can be relevant for the long-term stability of the catalyst.

### 3. Discussion

How does our approach compare with other methods for quantifying the degree of chlorination? So far, mostly Rietveld...
analyses of XRD data have been employed to quantify the bulk chlorination of CeO$_2$-based catalysts. This method is only applicable if hydrated CeCl$_3$ is crystalline. Fortunately, this happens to be the case for fully deactivated CeO$_2$-samples, although the X-ray amorphous part is unknown. However, XRD is not applicable for determining the degree of chlorination of a stable catalyst. Here, X-ray photoemission spectroscopy (XPS) can estimate the degree of chlorination of a stable CeO$_2$-based catalyst, although this method is not quantitative. From previous XPS studies, there is evidence that the chlorination degree is higher than just a surface coverage of chlorine for pure CeO$_2$ would presume. TGA together with mass spectrometry can be utilized for quantifying the degree of chlorination without relying on crystallinity of the chloride. However, all three methods suffer from being ex-situ in that the chlorinated catalyst has to be removed from the reactor in order to quantify its degree of chlorination.

Prompt Gamma Activation Analysis (PGAA) is particularly useful for the quantification of the chlorination degree since it can work even under reaction conditions or at least in situ in the reactor. PGAA has mostly been employed for biological systems, albeit it is not restricted to such systems. PGAA is quantitative and sensitive, but it requires a neutron source that rules out this method for standard analysis. Both Ce and Cl concentration can be determined separately and therefore the molar ratio Cl/Ce. The uncertainties for quantifying the degree of chlorination are small so that even differences in chlorination degree of the catalysts of a few mol% as a function of the reaction mixture can be determined. The drawback of PGAA is its relatively long data acquisition time (typically 1–2 h time) so that the kinetics of the reoxidation process during reactivation is not accessible.

The present in situ approach using UV-Vis detection in the Deacon reactor is fast and sensitive (ca. 1/10 monolayer), so that it is able to resolve the kinetics of the reoxidation step. Our approach is however not operando, since it requires a switch of the reaction mixture. Therefore, firm conclusions about the active phase cannot be drawn, although conclusions about the reactivation process of the catalysts are clear-cut.

It has been recognized that CeO$_2$-based catalysts deactivate in the Deacon reaction through bulk chlorination. There is also clear evidence that stoichiometric CeOCl is catalytically not active at all. Figure 8 summarizes the chlorination and oxidation of the pure (top) and supported catalysts (bottom) in a scheme. The deactivation of pure CeO$_2$ (top) leads to 70% chlorination, but the catalyst can be reactivated under reaction conditions with excess oxygen in the reaction feed at reaction temperatures of typically 430°C. Here we show that the restoration of bulk-chlorinated CeO$_2$ is almost quantitative. Through quantification of the reoxidation peak during the first reactivation cycle of deactivated CeO$_2$, we obtain a chlorination degree of 77%. A very similar value was determined by Rietveld refinement of XRD patterns for the deactivated CeO$_2$ samples, namely 76%. The coexistence of hydrated CeCl$_3$ and CeO$_2$ in deactivated CeO$_2$ can equally be verified by the Raman spectroscopy and XPS. This finding can possibly be explained by CeCl$_3$ particles blocking the surfaces of CeO$_2$ as indicated in Figure 8 (top), thereby preventing further chlorination. Subsequently, we evaluated the catalytic activity of reactivated CeO$_2$ under the mild Deacon condition. The activity of reactivated CeO$_2$ is 17% lower than that of the fresh one. From XRD it is evident that the CeO$_2$ particles have significantly grown in size after reactivation. Particles with smaller initial size may have disappeared more quickly upon chlorination than larger particles as indicated in Figure 8. Upon reoxidation, the growth of residual oxide particles is kinetically favored over nucleation of new particles, consistent with the low nucleation rate obtained in fitting the experimental reoxidation kinetics. The increase of the CeO$_2$ particle size concomitant with a smaller active surface area could be the reason for the observed decline in the steady state activity of CeO$_2$. The quantification of the second reoxidation peak yields a chlorination degree of 72%. The decline of the chlorination degree compared to the first time (77%) is rationalized by the growth of larger CeO$_2$ particles that are less prone to be chlorinated. The catalytic activity of CeO$_2$ after the second reactivation is 6% lower than after the first reactivation. This finding suggests that the deactivation/
reactivation process facilitates progressive sintering of the active component CeO\textsubscript{2}.

So far, no reactivation experiments for 20CeO\textsubscript{2}@ZrO\textsubscript{2} have been reported. From the first reoxidation Cl\textsubscript{2} peak of deactivated CeO\textsubscript{2} (Figure 3) we determine the chlorination degree of 20CeO\textsubscript{2}@ZrO\textsubscript{2} to be 100 \%, i.e., all CeO\textsubscript{2} is transformed to hydrated CeCl\textsubscript{3} \_nH\textsubscript{2}O consistent with Rietveld refinement of corresponding XRD data. The Raman spectrum and XPS of deactivated 20CeO\textsubscript{2}@ZrO\textsubscript{2} agree that the active ceria component in 20CeO\textsubscript{2}@ZrO\textsubscript{2} is fully chlorinated. As observed in TEM images of the deactivated catalyst (Figures 5a, b), the CeCl\textsubscript{3} phase is dispersed over the ZrO\textsubscript{2} surface as indicated in Figure 8 (bottom). Moreover, the reactivation of 20CeO\textsubscript{2}@ZrO\textsubscript{2} proceeds substantially faster than for pure CeO\textsubscript{2} due to the fine CeCl\textsubscript{3} dispersion and high nucleation rate of CeO\textsubscript{2} on the support surface. The activity of the 20CeO\textsubscript{2}@ZrO\textsubscript{2} sample after the first reactivation is only 8 \% lower than that of the fresh one. From the XRD experiments we know that during the first cycle the attached CeO\textsubscript{2} particles grow in size (XRD) consistent with a stronger ceria peak intensity in the Raman spectrum. TEM reveals that the CeO\textsubscript{2} wetting layer is fully recovered after reactivation (Figure 5c, d) and takes over most of the catalytically active phase. After the second deactivation step, the chlorination degree is only 91 \%, which can be attributed to the increase of the CeO\textsubscript{2} particle size as also reconciled with the Rietveld refinement. After the second reactivation step the sample recovers 99 \% of its catalytic activity. Therefore, we infer that the activity of the 20CeO\textsubscript{2}@ZrO\textsubscript{2} catalyst will be stable and not reduced after further “deactivation-reactivation” cycles.

In order to understand the restoration of the 20CeO\textsubscript{2}@ZrO\textsubscript{2} morphology and the full recovery of the activity after reactivation, we presume that the formed CeCl\textsubscript{3} \_nH\textsubscript{2}O particles need to adhere to the ZrO\textsubscript{2} support with high dispersion. This presumption is confirmed by TEM images (cf. Figures 5c, d). When subsequently the deactivated 20CeO\textsubscript{2}@ZrO\textsubscript{2} catalyst is exposed to oxygen, the adhering CeCl\textsubscript{3} \_nH\textsubscript{2}O layer transforms back to a thin covering layer of CeO\textsubscript{2} on ZrO\textsubscript{2} without significantly changing the morphology. The constraint of CeCl\textsubscript{3} \_nH\textsubscript{2}O adhering to the ZrO\textsubscript{2} surface restricts the mass transport to surface diffusion on the ZrO\textsubscript{2} surface and keeps the active surface area of exposed CeO\textsubscript{2} constant after reactivation.

It is evident that reactivation for pure CeO\textsubscript{2} takes much longer than that for 20 mol \% CeO\textsubscript{2} supported on ZrO\textsubscript{2} (cf. Figure 9). In addition, we observe different shapes of the Cl\textsubscript{2} signals during reoxidation. For a more quantitative description, we employ a phenomenological model based on the JMAK approach where a phase transformation is modeled by a nucleation and growth mechanism. In addition, we need to take into account the different starting conditions in the two samples. Fitting different parameters for the nucleation rates for pure CeO\textsubscript{2} and 20CeO\textsubscript{2}@ZrO\textsubscript{2} results in a nucleation rate that is 32 times higher for 20CeO\textsubscript{2}@ZrO\textsubscript{2}. The result can be explained by the high initial dispersion of CeCl\textsubscript{3} and the inert ZrO\textsubscript{2} surface providing nucleation sites for the growth of CeO\textsubscript{2}. While only 75 \% of the catalyst is chlorinated in the pure CeO\textsubscript{2} samples, the fitted nucleation rate is substantially lower, possibly indicating

![Scheme of chlorination and reoxidation and subsequent particle agglomeration for the pure CeO\textsubscript{2} catalyst (top) and the supported CeO\textsubscript{2}@ZrO\textsubscript{2} catalyst (bottom).](image1)

![Time needed for reactivation of CeO\textsubscript{2} in comparison to that of 20CeO\textsubscript{2}@ZrO\textsubscript{2} after the activity measurement of fully-deactivated state.](image2)
that the CeO$_2$ surface contributes less to nucleation. This assumption is consistent with the earlier conclusion that the surface of residual CeO$_2$ is entirely covered by CeCl$_3$ after chlorination (and thereby not available as a site for oxide nucleation), thereby suppressing complete chlorination.$^{[11]}$

Finally, we raise the question why the CeO$_2$ layer on ZrO$_2$ is always restored during reoxidation. While higher stability of the CeO$_2$ film grown on ZrO$_2$ compared to CeO$_2$ particles may be one possible explanation for the reversible film restoration, we currently have no insight into the relative (thermodynamic) stabilities of the CeO$_2$ film on ZrO$_2$ versus CeO$_2$ bulk particles. However, our fitted nucleation rate constants suggest that nucleation appears to be faster when the ZrO$_2$ surface is exposed. The support surface may thereby aid in the redistribution of the catalyst upon reoxidation.

Our kinetic model for the reoxidation could be further refined by considering additional steps of the reaction and different nucleation sites and growth modes of the formed CeO$_2$ films and particles, for instance, in the form of a Kinetic Monte Carlo model.$^{[20]}$ However, we cannot meaningfully fit more parameters to the available data. More detailed models to obtain deeper understanding of catalyst degradation and reactivation needs extended experimental data sets under various reaction conditions or a first-principles-based approach.

The deactivation/reactivation cycle of CeO$_2$ based catalysts in the HCl oxidation reaction can be considered as a redox reaction where the reduction and oxidation step is separated (similar to an electrochemical reaction). Actually in this kind of Born-Haber cycle, chlorine can be produced within a cycle of solid state reactions: metal oxide is chlorinated first to form metal chloride (exothermic) and then in a separate chamber the metal chloride is reoxidized (endothermic) to release the desired product Cl$_2$ and to recover the metal oxide.$^{[4,6]}$ Therefore, we can ask ourselves how important is the chlorine release in the reoxidation of the CeO$_2$-based catalyst for the overall conversion of HCl. For the active and stable catalyst, there is only little chlorine at the surface. The replacement of this chlorine species by oxygen amounts only to about 20% of the reached rate under steady state Deacon conditions (cf. Figure 6). Therefore, this contribution is likely to be not relevant for the overall conversion, although it is important for the chemical nature of the catalytically active phase.

### 4. Conclusion

Pure CeO$_2$ and 20 mol% CeO$_2$ supported on preformed ZrO$_2$ particles (20CeO$_2$@ZrO$_2$) fully deactivate under harsh HCl oxidation conditions by the formation of Ce bulk chlorides. With an oxidative step in a pure oxygen atmosphere the deactivated catalysts can be reactivated by reoxidation and the replaced chlorine can be quantified in-situ by the UV-Vis analytics in the flow reactor. The catalytic activity of 20CeO$_2$@ZrO$_2$ is completely recovered after the second deactivation/reactivation cycle, while the activity of pure CeO$_2$ after reactivation declines steadily. UV-Vis data acquisition is fast so that the kinetics of the reactivation step via the reoxidation can readily be followed and be used to model the solid-state reaction mechanism of the dechlorination reaction of hydrated CeCl$_3$ by oxygen. With a simple nucleation and growth model based on the JMAK approach, the different reoxidation kinetics of the two samples can be explained by high nucleation rate of CeO$_2$ on the ZrO$_2$ support surface. While the ZrO$_2$ surface is otherwise inert in the HCl oxidation reaction, it appears to provide sites for the nucleation of CeO$_2$ particles and keeps CeCl$_3$ particles in the chlorinated catalyst dispersed. The ZrO$_2$ support thereby aids in the redispersion of the catalyst during chlorination-dechlorination cycles. We conclude that the choice of catalyst support is crucial to prevent catalyst deactivation in non-steady-state operation.

The UV-Vis analytics is very sensitive so that even the chlorination degree of stable catalysts can be quantified with values that are in close agreement with those derived from PGAA experiments. The chlorination degree of stable catalysts is significantly higher than expected from a bare Cl overlayer with severe consequences for the reaction mechanism and hence for its theoretical modeling.

We propose that in-situ deactivation and reactivation experiments, coupled with an accurate quantification of the degree of transformation and theoretical modeling can be used to gain a detailed understanding of how the support alters the stability and activity of catalyst required to further improve catalyst-support combinations. In principle, this kind of in-situ experiments can be employed whenever the product or the educt is able to transform the chemical (bulk) composition of catalyst, thus opening the door for further experiments and scientific questions.$^{[10]}$

### Author contribution

Y. Sun prepared the materials and conducted the experiments and wrote a first draft. F. Hess developed the reoxidation model and performed the theoretical analysis. I. Djerdj performed the Rietveld analysis. T. Weber conducted the XPS experiments and analyzed the XPS data; Zhen Wang performed some of the activity experiments. H. Over conceived the original idea and took the lead in writing the manuscript with contributions from Y. Sun, F. Hess, and Bernd Smarsly.

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Conflict of Interest

The authors declare no conflict of interest.

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