Understanding CeO$_2$ as a Deacon catalyst by probe molecule adsorption and in situ infrared characterisations†

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CeO$_2$ has been identified as an efficient catalyst for HCl oxidation in the temperature range of 623–723 K provided that the oxygen content in the feed mixture was sufficiently high to avoid bulk chlorination and thus deactivation. Here we characterise ceria in its fresh and post-reaction states by adsorption of CO$_2$, NH$_3$ and CO. Micro-calorimetry, FTIR and TPD experiments are complemented by DFT calculations, which assess adsorption energies and vibrational frequencies. The calculations were performed on the lowest energy surface, CeO$_2$(111), with perfect termination and with various degrees of hydroxylation and/or chlorination. Both experiments and calculations suggest that the basic character of the ceria surface has been eliminated upon reaction in HCl oxidation, indicating that most of the basic lattice O sites are exchanged by chlorine and that the OH groups formed are rather acidic. The density and the strength of surface acidic functions increased significantly upon reaction. An in situ FTIR reaction cell has been designed and constructed to study the evolution of OH group density of the ceria surface during HCl oxidation. The effect of experimental variables, such as $p$O$_2$, phCl and temperature, has been investigated. We found that the OH group density positively correlated with the reactivity in the $p$O$_2$ and temperature series, whereas negative correlation was observed when phCl was varied. Implications of the above observations to the reaction mechanism are discussed.

Introduction

Chlorine is manufactured on the large scale by electrolysis of aqueous NaCl or HCl solutions. The heterogeneous catalysed gas phase HCl oxidation (Deacon reaction) over supported RuO$_2$ materials offers a viable alternative route to produce Cl$_2$. Despite its recent implementation, the quest for cheaper catalysts led to the recognition of CeO$_2$ as a highly stable HCl oxidation catalyst. Our performance and characterisation results showed that mildly high-temperature (1173 K) calcined material represents an optimum between stabilised surfaces and unacceptable loss of surface area. The surface of ceria is chlorinated during the reaction and inactive cerium chloride may form when the oxygen over-stoichiometry of the reaction feed is low. As opposed to the metallic nature of RuO$_2$, ceria requires redox chemistry and thus oxygen vacancies impact the catalytic activity. In a simplified view, the mechanism of Deacon reaction involves reactive HCl adsorption via proton abstraction in the formation of OH and surface Cl, recombination of these species (H$_2$O and Cl$_2$) and surface re-oxidation by dissociative oxygen activation. It is suggested that several of these steps require an anionic vacancy.

Infrared spectroscopy (FTIR) offers the possibility to characterise surface acid/base properties that can be regarded as a crucial parameter in the adsorption energetics but also in the surface reaction steps of HCl oxidation. Moreover, infrared techniques enable observation of surface species under reaction conditions. In situ studies of surface species using FTIR, determination of surface sites and the various cell designs available for these studies have been recently reviewed. Ceria is used as a carrier or an additive in various catalytic processes, and in situ FTIR has been regularly utilised to extract...
mechanistic details in reactions such as the water–gas shift, reverse-WGS, low-temperature CO oxidation, and PROX. In situ FTIR studies on ceria as the main catalytic material are, however, much scarcer. In this manuscript, we aim at understanding how the surface acid/base properties of fresh ceria are modified by HCl oxidation. For this purpose, FTIR and micro-calorimetric characterisation of probe molecules (CO2, NH3 and CO) in combination with DFT calculations have been applied. Furthermore, we have designed an in situ FTIR cell to study ceria under Deacon reaction in the transmission geometry. This cell withstands the corrosive ambient conditions represented by the reaction gas mixture containing HCl, O2, Cl2 and H2O. In the in situ experiments we tried to quantify OH groups formed under HCl oxidation and understand their role in the overall mechanism.

Experimental

Sample

Unsupported CeO2 (Aldrich) was calcined in static air at 1173 K (10 K min\textsuperscript{-1}) for 5 h. This sample, either as fresh (hereafter denoted CeO2-F) or after Deacon reaction (treated under various feed conditions, ending with HCl : O\textsubscript{2} = 1 : 9 at 593 K, hereafter denoted CeO2-D) was used for characterisations.

HRTEM characterisation

High resolution transmission microscopy with aberration correction (FEI Titan Cs 800–300) was utilised to assess the morphology of the ceria particles.

NH3 temperature programmed desorption

NH3-TPD was measured in a Thermo TPDRO 1100 unit equipped with a thermal conductivity detector. The samples (300 mg) were loaded in the quartz micro-reactor (11 mm i.d.), pre-treated in He (20 cm\textsuperscript{3} STP per min) at 573 K for 3 h, and cooled to 373 K in He. NH3 was chemisorbed at 373 K in three consecutive cycles of saturation with 10 vol\% NH3/He (20 cm\textsuperscript{3} STP per min) for 30 min followed by purging with He (20 cm\textsuperscript{3} STP per min) at the same temperature for 30 min. Desorption of NH3 was monitored in the range of 323–1273 K using a heating rate of 20 K min\textsuperscript{-1} and a He flow of 20 cm\textsuperscript{3} STP per min.

Micro-calorimetry

Micro-calorimetric experiments were carried out in a Calvet calorimeter (SETARAM MS70) combined with a high vacuum system, which enables the dosage of probe molecules within a range of 0.02 μmol. The samples were pre-treated according to the following procedure: CeO2-F was exposed to synthetic air at 773 K for 5 h, whereas CeO2-D (after Deacon) was only degassed under UHV at 423 K for 5 h. The pre-treatment was conducted in a separate chamber connected to the calorimetric cell. The final pressure in the degassed cell was approximately 10\textsuperscript{-6} mbar. The cell was cooled to room temperature, placed inside the calorimeter, and connected to the micro-calorimetric gas-adsorption system. Subsequently, CO\textsubscript{2} or NH\textsubscript{3} was dosed stepwise at 313 K. Pressure, adsorption temperature, and the heat signals were recorded during all dosing and desorption steps. Desorption was performed at adsorption temperature under UHV. In all calorimetric sections positive energy corresponds to an exothermic process.

Probe molecule adsorption by FTIR

Fourier transform infrared (FTIR) spectroscopic measurements were carried out using a Perkin-Elmer PE100 spectrometer equipped with an MCT detector. The spectra were recorded with a resolution of 2 cm\textsuperscript{-1} and accumulation of 64 scans. Self-supported wafers were prepared by pressing the sample under a pressure of 230 bar. The samples were activated first in situ prior to IR measurements. The cell is connected to a vacuum system with a residual pressure of ca. 1 x 10\textsuperscript{-7} mbar. A background spectrum of the empty cell was used to subtract the CO adsorption spectra of the sample. CO was initially dosed at 77 K up to equilibrium pressure (1.86 mbar for non-chlorinated and 1.31 mbar for chlorinated ceria). Then, the gas was evacuated in sequential steps in order to study the coverage dependence.

In situ FTIR in HCl oxidation

An in situ transmission FTIR cell (Fig. 1) has been designed to enable investigating Deacon catalysts under reaction conditions. Details of the cell design will be discussed in the Results section. A CeO2-F sample was pressed into a self-supporting disc (31.8 mg cm\textsuperscript{-2}) and placed in the sample holder in the center of the furnace of the IR cell. The sample was heated in flowing synthetic air up to 723 K (10 K min\textsuperscript{-1}) and allowed to stabilise for 90 min. Spectra were recorded using a Varian-670 FTIR spectrometer under the reaction conditions indicated. A resolution of 4.0 cm\textsuperscript{-1} was used throughout the investigation and in most cases 512 scans were averaged to achieve a satisfactory signal-to-noise ratio. Reactivity was followed by means of iodometric titration. Reaction feed, at constant 100 cm\textsuperscript{3} STP per min total flow, was supplied by mass flow controllers. The Deacon reaction was started in an oxygen-rich atmosphere with a feed composition HCl : O\textsubscript{2} : N\textsubscript{2} = 1 : 9 : 0 at 703 K. The reaction was maintained under this condition for 16 h before starting to investigate the effects of various reaction conditions (p\textsubscript{n}, T). During the O\textsubscript{2} partial pressure dependence, the HCl flow was kept constant at 10 cm\textsuperscript{3} STP per min and the O\textsubscript{2} flow was varied according to the following feed composition sequence: HCl : O\textsubscript{2} : N\textsubscript{2} = 1 : 9 : 0, 1 : 4 : 5, 1 : 2 : 7, 1 : 1 : 8 and 1 : 0.5 : 8.5. During the measurement of HCl partial pressure dependence, the O\textsubscript{2} flow was kept constant at 20 cm\textsuperscript{3} STP per min and the HCl flow was changed as follows: 10, 6, 3 and 1 cm\textsuperscript{3} STP per min. The time interval for each of the above steps was ~5 h, and the temperature was kept constant at 703 K. The temperature effect was studied at an oxygen-rich feed composition of HCl : O\textsubscript{2} : N\textsubscript{2} = 1 : 9 : 0 by reducing the temperature, stepwise by 20 K, starting from 703 K and ending at 623 K. The time interval for each step was ~4 h.
Density functional theory calculations of probe molecule adsorption

Density functional theory (DFT) simulations have been applied to CeO$_2$ slabs. The calculations were performed with the 5.2.12 version of the VASP code.$^{25}$ The functional of choice was PBE+U,$^{26}$ to partially account for self-interaction issues in the f-electrons. The U parameter chosen was set to 4.5.$^{27-29}$ Inner electrons were replaced by PAW pseudopotentials$^{30}$ while the 12 valence electrons of Ce atoms in the 5s, 5p, 6s, 4f, 5d states and the 6 valence electrons of O atoms were considered explicitly. The valence electrons were expanded in plane waves with a cut off energy of 400 eV. For further details the reader is referred to ref. 8. The lowest energy surface, CeO$_2$(111), was taken as representative of the material. The chosen slab corresponds to a $p(2\times2)$ reconstruction and contains 3 layers. The $k$-point sampling was set to $5 \times 5 \times 1$.Slabs were interleaved by 10 Å and artificial polarisation interactions due to the asymmetry of the adsorption configuration were removed by standard procedures. Spin polarised calculations were performed when needed. Vibrational frequencies were calculated through the diagonalisation of the numerical Hessian obtained by displacements of $\pm 0.02$ Å for each degree of freedom. A description of how good theoretical methods are at analysing acid–base properties of surfaces can be found elsewhere.$^{32}$ The full tables with adsorption energy and frequency calculations and spin states are presented in the ESI† and only the most representative features are described in the main text.

Results and discussion

HRTEM

HRTEM analysis of the CeO$_2$-F sample mostly revealed well faceted particles in the range of 20–50 nm with a few larger particles around 100 nm (Fig. 2). Many particles show (111) lattice fringes with a well faceted surface, suggesting the formation of energetically stable surface orientations. The sample after 80 h in the Deacon reaction revealed some changes in the morphology of the particles. The overview micrographs show the relatively broad particle size distribution being conserved, though many of the sharp corners of the CeO$_2$ particles seem to be smoothed and rounded upon the reaction. Despite the smoothening of edges, the crystalline structure remains that of CeO$_2$.

Micro-calorimetry and corresponding DFT analysis

The pressure-controlled dosing system of the calorimeter with calibrated volume enables the quantification of adsorbed molecules (adsorption isotherm) as well as the differential heat of adsorption and gives the possibility to elucidate the distribution of the adsorption sites along the range of adsorption heats. These results (Fig. 3) are compared with the modelling obtained through DFT in order to unravel the nature of the adsorption sites.

It has been shown that the Deacon reaction gives rise to surface chlorination,$^8$ thus, it is expected that acid–base properties of the surface are modified. Ceria is an amphoteric compound showing both surface acidity and basicity. Therefore, NH$_3$ and CO$_2$ probe molecules were used to assess acidic and basic properties of the samples, respectively, before and after reaction. For comparison, calculations were performed on different models representing the local structures in Fig. 4. Adsorption of probe molecules using DFT calculations has been performed on a model CeO$_2$ (111) surface and with different degrees of hydroxylation and/or defects involved, Fig. 4 (For the configurations with adsorbates see Fig. S1, ESI†). Finally, a summary with the
assignments based on either adsorption energies or frequencies is proposed (Table 1).

CO₂ adsorption was performed at 313 K in order to derive information from the pure adsorption process by suppressing secondary reactions, which have been shown to occur at higher temperatures. The results are depicted in Fig. 3A and B. The differential heat of adsorption profile as a function of CO₂ uptake for the CeO₂-F demonstrates energetically wide distribution of basic interacting sites. Nevertheless, two distinct sites exhibited uniformity, as can be recognised by two plateaus at very low and relatively high pressures (Fig. 3B). The amount of these two energetically homogeneous sites (ca. 7 μmol g⁻¹ CO₂ adsorbed for each plateau) is small in comparison to the whole available basic sites on the surface. The initial heat of adsorption is about 110 kJ mol⁻¹. These adsorption energies were suggested to correspond to structural defects such as edges in nanoparticles or vacancies in more open facets such as (110). In our calculations, multiple (3) CO₂ adsorption on a single vacancy site could account for a large average adsorption energy >100 kJ mol⁻¹ (see Table S3, ESI†). The adsorption energy profile in Fig. 3B decreases gradually with coverage until reaching the second plateau at about 55 kJ mol⁻¹. This energy plateau can be assigned to the formation of carbonate species (our calculation: 43 kJ mol⁻¹) with the basic O atoms on the surface (Fig. S1(i), ESI†). In Fig. 3B, a small amount of CO₂ adsorbed with lower heat of adsorption values. Indeed, the calculations show that the interaction with partially hydroxylated surfaces is weaker (18 kJ mol⁻¹ and lower) and similar values are retrieved for oxygen vacancies when one of the O atoms of the CO₂ molecule fills the vacancy. Repeated adsorption experiment after desorption (at 313 K, UHV) revealed a certain degree of irreversible adsorption; either related to strong adsorption on low coordination sites and/or carbonate formation. The decrease of the heat of adsorption at the first plateau may be explained by the repulsive interaction of CO₂ with the irreversibly adsorbed species. By considering the wide range of heats of adsorption, it can be conveniently concluded that both Lewis and Brønsted basic sites are present in the non-chlorinated sample.

In contrast to CeO₂-F, CO₂ does not show any considerable interaction with the chlorinated surface, even at relatively high CO₂ pressures (Fig. 3A). Indeed, very weak adsorption energies were calculated on the models for the partially chlorinated
Therefore, we can confidently infer that during the reaction CeO$_2$ lost basicity due to surface chlorination and acidic hydroxyl formation (detailed in later sections). In other words, the population of Lewis sites seems to be greatly attenuated$^{16}$ and that of Bronsted sites (OH groups) does not possess basic properties anymore.

NH$_3$ was employed to investigate acidic properties of the samples. Due to stainless steel tubing applied in our microcalorimetric setup, the determination of the initial differential heat of adsorption values was not straightforward. Hence, initial values at very low NH$_3$ pressures were not analysed. The ammonia adsorption results are illustrated in Fig. 3C and D. The chlorinated sample gave rise to enhanced interaction up to $\sim$150 $\mu$mol g$^{-1}$ adsorption, after which both samples reach a plateau at $\sim$25 kJ mol$^{-1}$. The isotherm and heat of adsorption values demonstrate an increased acidity of the chlorinated surface. Re-adsorption evidences a significantly higher amount ($\sim 3\times$) of irreversibly held ammonia on the sample after Deacon reaction. The concomitant presence of high proton density, leading to a larger number of NH$_4^+$ groups, and high polarisability of the chlorine atoms on the surface that increases the electrostatic interactions can be responsible for the enhanced ammonia adsorption in the post-reaction sample.
Table 1  Summary of the experimental and calculated adsorption, $E$ in kJ mol$^{-1}$, and vibrational frequencies, $\nu$ in cm$^{-1}$, of probe molecules together with the corresponding model

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E^{exp}$</th>
<th>$E^{calc}$</th>
<th>$\nu^{exp}$</th>
<th>$\nu^{calc}$</th>
<th>Species</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>110</td>
<td>55</td>
<td>43</td>
<td>1593</td>
<td>CO$_{2-}$</td>
<td>Multiple adsorption at vacancies</td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td>1394</td>
<td></td>
<td>1416–1382</td>
<td>NH$_4^+$</td>
<td>Regular surf.</td>
</tr>
<tr>
<td></td>
<td>1557</td>
<td>50</td>
<td>1593–1566</td>
<td></td>
<td>CO$_{2-}$</td>
<td>Bronsted</td>
</tr>
<tr>
<td></td>
<td>1414</td>
<td></td>
<td>1615–1612</td>
<td></td>
<td>NH$_4^+$</td>
<td>Lewis</td>
</tr>
<tr>
<td>CO</td>
<td>2155</td>
<td></td>
<td>2112</td>
<td></td>
<td>NH$_4^+$</td>
<td>Chlorinated surface</td>
</tr>
<tr>
<td></td>
<td>2161</td>
<td></td>
<td>2127</td>
<td></td>
<td>[O$_{\text{lattice}}$H]</td>
<td>(O$_{\text{lattice}}$H · OH) chlorinated</td>
</tr>
<tr>
<td></td>
<td>2186</td>
<td></td>
<td>2157</td>
<td></td>
<td>[O$_{\text{lattice}}$H · Cl]</td>
<td></td>
</tr>
</tbody>
</table>

FTIR spectra for ammonia adsorption on fresh and chlorinated samples (not shown) also reveal a stronger interaction of NH$_3$ with the chlorinated sample, as the peaks that are believed to correspond to the interaction with Bronsted (1396 cm$^{-1}$) and Lewis (1557 cm$^{-1}$) acid sites are both shifted to the higher frequencies in this case. This is indeed seen from the calculations as the direct interaction to Ce$^{4+}$ sites is calculated to give a main peak at 1593 cm$^{-1}$, which shifted upon chlorination to 1615–1612 cm$^{-1}$. Other bands in the same region may correspond to NH$_3$ adsorption to hydroxyl groups on the surface, 1566, 1562 (CeO$_2$H) and 1583 cm$^{-1}$ (CeO$_2$H–OH).

The acid strength distribution on the CeO$_2$ samples related to the irreversible NH$_3$ adsorption in the micro-calorimetry was studied further by NH$_3$-TPD in the range of 323–1273 K (Fig. 5). The distribution of acid sites on the fresh CeO$_2$ is broad, indicating the presence of both medium and strong acid sites. The medium acid sites appear to be much more abundant than strong ones. These results are in good agreement with the previous literature reporting on the acidity/basicity of rare-earth oxides. For the CeO$_2$-D sample a new TPD peak centered at ca. 555 K and a large peak in the broad range of 800–1000 K appeared. These peaks cannot be due to chlorine desorption from the catalyst surface as the TGA-MS analysis showed a very small amount of chlorine leaving the surface (in the range of 500–660 K, Fig. S2, ESI$^\dagger$). Accordingly, these peaks are attributed to the generation of new medium and strong acid sites during HCl oxidation. Integration of the TDS signal yields an approximately 3-times higher response for the CeO$_2$-D sample in good agreement with the observed ratio of irreversible NH$_3$ adsorption by microcalorimetry (see Fig. 3C).

When comparing to the computed results, within the PBE+U approach, the adsorption of ammonia with the N-down configuration on the Ce$^{4+}$ site of the undefective surface is 50 kJ mol$^{-1}$ (see Fig. S1(e), ESI$^\dagger$). A second configuration with the three H atoms interacting with 3 neighbouring Lewis basic sites, i.e. O anions, leads to mere 9 kJ mol$^{-1}$. Adsorbed on Bronsted acids (OH models), the adsorption is slightly weaker (31–39 kJ mol$^{-1}$). Using the model with partial chlorination and concomitant neighbouring Bronsted (OH) sites on the surface the interaction is stronger (about 60 kJ mol$^{-1}$) in agreement with the experimental observations. These values are somehow smaller than the 500 K desorption peak would indicate, but they will be largely affected by the coordination of the Ce$^{4+}$ cations. It is likely that the structure at higher desorption temperatures found in TPD arises from breaking the NH$_4^+$ binding to the surface (see Table S2, ESI$^\dagger$ for the configurations). With surface hydroxylation two different configurations may exist: one with OH · NH$_3$ interactions, where the H is still bonded to oxygen on the surface, or ammonia can strip the H from some of these centers to generate NH$_4^+$ species that can wander on the surface (see e.g. Fig. S1(g), ESI$^\dagger$). Electrostatic interaction of NH$_4^+$ with polarised surface Cl will further strengthen ammonia adsorption. The elimination of this species in the form of ammonia likely requires more energy than any other NH$_3$ desorption process, but it is unfortunately not well-reproduced by the calculations due to the charge displacement, the total charge state and the periodic boundary conditions employed in the simulations.

Probe molecule adsorption by FTIR and corresponding DFT analysis

CO is one of the most frequently used probe molecules in IR spectroscopy. Owing to its specific properties (sensitivity, accessibility and high extinction coefficient) crucial information can be obtained in terms of identification of adsorbing sites (Bronsted and Lewis) and definition of oxidation states. In comparison to experiments, the DFT calculations underestimate the CO stretching frequency and thus only shifts are usually discussed to analyse...
the results. It is worthwhile mentioning here that the σ-bond and electrostatic interactions cause hypochromic frequency shifts, and the electrical field strength of metal ions is not only dependent on the formal charge but also the contribution of the metal ions’ environment to the effective charge must be taken into account.\(^3\) Hence, the effect of surface chlorination on the acid–base properties was further studied by monitoring shifts of CO vibrational frequencies at 77 K on both fresh and chlorinated samples. The former was pre-treated in batch at 200 mbar oxygen and 823 K for 5 h, O\(_2\) had been replaced every 30 min to prevent re-adsorption of desorbing contaminants. The chlorinated sample was pre-treated in O\(_2\) (200 mbar) at only 473 K for 5 h, as the surface after chlorination and thus replacement of O\(^{2-}\) anions is now less prone to the formation of carbonate species.\(^3\) Further, this minimises dechlorination. The samples were subsequently evacuated during cooling down. CO adsorption spectra on CeO\(_2\)-F are shown in Fig. 6a. After equilibration with 1.86 mbar CO at 77 K, two close and overlapping peaks at 2150 and 2155 cm\(^{-1}\) with two shoulders at 2172 and 2140 cm\(^{-1}\) appeared.

Taking the IR frequency of gas phase CO (2143 cm\(^{-1}\)) as a reference, we can attribute the aforementioned bands and shoulders as follows: (i) the shoulder at 2140 cm\(^{-1}\) can be assigned to the physisorbed CO, since it is the closest one to the reference value, and it desorbs easily upon evacuation, (ii) the band at 2150 and 2155 cm\(^{-1}\), which are slightly up-shifted, can be attributed to CO hydrogen-bonded to OH groups of different acid strengths. This carbonyl band is accompanied by intensity perturbation and redshift of the ν(OH) bands (see the inset in Fig. 6a). Further evacuation gives rise to the disappearance of the band at 2150 cm\(^{-1}\), which seems to have weaker interaction with the surface OH groups, whereas the band at 2155 cm\(^{-1}\) was decreasing gradually and shifting to higher wavenumbers with increasing vacuum. This shift is attributed to the diminishing intermolecular interactions at lower coverage.\(^2\) By considering CO as a weak electron donor molecule, the higher the positive shift of Δ(CO), the stronger is the interaction with surface sites. The minor shoulder at 2172 cm\(^{-1}\) can be assigned to the CO interaction with Ce\(^{4+}\) sites,\(^4\) in agreement with the stronger adsorption of CO on the cationic site. However, DFT adsorption energies on cus Ce\(^{4+}\) is mere 18 kJ mol\(^{-1}\), and therefore this band is more likely related to adsorption on more open surface sites.

Calculations are not fully conclusive at this stage. Indeed, adsorption energies have previously been calculated with different approximations leading to a range of 16–25 kJ mol\(^{-1}\),\(^4\) and the presence of hydroxyl groups, although induces CO shifts of +40 cm\(^{-1}\), reduces the adsorption energy further (O\(_{\text{ lattice}}\)H model). Partially water covered surfaces (the CeO\(_2\)-OH water pair model) might be responsible for stronger adsorption, about 48 kJ mol\(^{-1}\), with the CO shift being dependent on the type of surface site (lattice or on top OH) CO interacting with (see Table S4, ESI†). The frequency shift is about +10 cm\(^{-1}\) when adsorption takes place close to the Ce\(^{4+}\) cations.

FTIR spectra of CO adsorption on chlorinated sample are illustrated in Fig. 6b. The main peak at high coverage is situated at 2161 cm\(^{-1}\). According to the calculations this can be assigned to CO interacting with hydroxyls on the surface where the CO molecule is basically sitting with the C-down close to a Ce atom (see Fig. S1(o), ESI†). As these sites are not blocked in the Deacon reaction they seem to be rather stable when compared to the clean surface. There is an additional shoulder at 2144 cm\(^{-1}\) and a small band at 2186 cm\(^{-1}\). Upon evacuation, the band at 2144 cm\(^{-1}\), which is very close to the gas phase ν(CO) disappeared. At lower pressures, the intensity of the main band further decreases and shifts to the higher wavenumber and splits up into two peaks. All bands, with exception of physisorbed CO at 2144 cm\(^{-1}\), are blue shifted by ~10 cm\(^{-1}\) in comparison with those from the non-chlorinated sample. This blue shift indicates an overall increase of the acidity of the surface upon chlorination. The extent of the redshift of the OH band upon interaction with CO (inset in Fig. 6a) has often been utilised to evaluate the strength of surface Brønsted acid sites.\(^3\) The magnitude of OH

**Fig. 6** (A) FTIR spectra of CO adsorbed at 77 K on fresh CeO\(_2\); after admission of 1.860 mbar CO in equilibrium (black-spectrum), after various sequential steps of evacuation (rest). Inset: the difference spectrum of the sample before and after admission of CO; (B) FTIR spectra of CO adsorbed at 77 K on CeO\(_2\)-D; after admission of 1.306 mbar CO in equilibrium (black-spectrum), after sequential steps of evacuation (rest). Inset: zoom in for the band at 2186 cm\(^{-1}\).
shifts was $\sim 75$ cm$^{-1}$ for the fresh CeO$_2$. The calculated value for CO-induced shifts of O$_{\text{lattice}}$H is about 100 cm$^{-1}$. Whereas, it is in the range between 137 and 164 cm$^{-1}$ for ceria after Deacon reaction, corroborating the enhanced acidity of the Bronsted sites. This latter value is not reproduced in the calculations and one of the reasons for the discrepancy might be high surface water content.

**In situ FTIR under Deacon reaction**

**Cell design.** For a successful in situ cell design, several aspects should be taken into consideration, such as small void volume, suitable IR-windows and construction materials, especially when it comes to such highly corrosive gaseous conditions, as for the Deacon reaction.

Our cell (Fig. 1) consists of two main parts. The cell body is provided with two IR transparent Si windows and two 1/8 in. tubing for the inlet and outlet of the reactant gases and products. Si windows (20 mm id, 1 mm thickness) were fixed between two PTFE gaskets and sealed with Kaltrez o-rings, which are chemically resistant at relatively high temperatures. The body of the cell is made of stainless steel; however a galvanic silver coating was applied on the inner walls. Silver is resistant to dry and moist chlorine at room temperature.

A compact film of silver chloride is expected to form during the galvanic silver coating was applied on the inner walls. Silver is resistant to dry and moist chlorine at room temperature. A compact film of silver chloride is expected to form during the exposure of silver to molecular chlorine. This chloride layer is responsible for the resistance of the silver.

The lid is provided with a cylindrical oven (sample holder) and thermocouple for monitoring the temperature of the sample. Hastelloy C-22 was used as constructing material for the lid, which is coated afterwards with a special inert Si-based coating (Silcolloy$^\text{TM}$ 1000) using the CVD procedure. The sample holder serves as the heating system that operates in the temperature range from 300 to 823 K. The internal volume of the cell is ca. 20 cm$^3$.

**In situ experiments.** It has been proposed recently$^8$ that the mechanism of the Deacon reaction on CeO$_2$ includes two elementary steps that describe the formation and consumption of OH groups during the reaction. These results were based on DFT calculations. IR spectroscopy is among the best spectroscopic techniques known for monitoring the changes of OH even if no plateau was reached even after 16 h on stream. This phenomenon may be interpreted based on structural evolution of the surface during the reaction, with sharp facets becoming more rounded.

HCl was introduced in the feed ratio HCl : O$_2$ = 1 : 9 at 703 K. Similar changes (Fig. 7) were observed at the early stages of the reaction as with the lower temperature calcined CeO$_2$ and strongly diluted Deacon feed.$^8$ Both OH bands at 3621 and 3700 cm$^{-1}$ have vanished upon HCl introduction, the band at 3730 cm$^{-1}$ was better resolved, and a broad band near 3500 cm$^{-1}$ developed. This latter is related to surface water.$^8$ A pronounced increase of the band at 3730 cm$^{-1}$ was observed in advanced stages of the reaction (see Fig. 7, black spectrum), whereas another low intensity band at 3676 cm$^{-1}$, which is observed only after introducing HCl into the feed, does not show remarkable variation with time. Since the initial changes under Deacon conditions were very fast, the single beam spectrum after 32 s on the Deacon feed (blue spectrum) was used as background to follow the evolution of the band at 3730 cm$^{-1}$. The time evolution of absorbance spectra was fitted (see Fig. S3, ESI$^\text{†}$ as an example) and we analyse the evolution of the abundance of the mono-coordinated OH component. The integral area of this peak at 3730 cm$^{-1}$ increased very rapidly at the beginning of the reaction (Fig. 8). Then, changes slowed down appreciably, though no plateau was reached even after 16 h on stream. This phenomenon may be interpreted based on structural evolution of the surface during the reaction, with sharp facets becoming more rounded.

The reaction conditions ($p_i$ and $T$) were varied individually to study the influence of each parameter on the concentration of the OH groups. Fig. 8 shows the integration data for the whole experiment, in which first $pO_2$, then $pHCl$ and lastly temperature was varied. Due to the non-steady nature of OH even after 16 h, we repeated the same reaction conditions twice to control the effect related to this. These data were fitted with a mathematical function and the actual OH abundance has been corrected with the hypothetical value given by the fit at the corresponding time on stream.

**O$_2$ dependence.** The effect of various $pO_2$ contents in the feed on the reaction rate level and the OH concentration compared...
to that in the standard feed of HCl : O₂ = 1 : 9 is illustrated in Fig. 9. Increasing oxygen content gives rise to increasing reactivity that can be fitted to a formal pO₂ dependence of ~0.4. In parallel, the OH concentration is the highest at the most oxygen rich feed and decreases continuously when pO₂ is lowered. The major changes in the OH concentration occur fast, usually within 2–3 min, thus the surface rapidly responds to the changes in the feed stream. In this experiment we observe a positive relationship between OH concentration and the reactivity, in the sense that higher OH coverage results in higher conversion.

HCl dependence. Before starting the investigation of pHCl dependence, the sample was reactivated by switching to O₂ rich feed compositions (HCl : O₂ = 1 : 4 then 1 : 9, 3 h for each), since feeds with low oxygen content were shown to induce deactivation.⁸

According to the proposed mechanism,⁸ HCl dissociation on the surface is a fundamental reaction step, which is responsible for the compensation of OH group’s loss during the formation of the by-product H₂O. Thus, one may assume that by reducing the inlet pHCl, OH concentration will decrease. Fig. 10 demonstrates exactly the opposite behaviour, that is, by reducing pHCl (from 10 to 1 cm³ STP per min in always constant 100 cm³ STP per min total flow) and keeping also pO₂ constant (20 cm³ STP per min), OH concentration has steadily increased. In parallel, the Cl₂ productivity decreased, and therefore in this experiment the higher reaction rate correlates with decreasing OH concentration.

T dependence. Temperature influence was studied by reducing the temperature stepwise (20 K for each step) in the range from 703 to 623 K. Decreasing reaction temperature induces a loss of activity according to the Arrhenius law. The calculated apparent activation energy is 70 kJ mol⁻¹. Fig. 11b indicates that decreasing temperature and reactivity correlates with lower OH concentration, similar to that found in pO₂ dependence.

Mechanistic considerations. Micro-calorimetric experiments with CO₂ adsorption suggested a loss of basic character of the ceria surface after reaction under Deacon conditions. That is, most of the basic lattice O surface sites are exchanged to surface (lattice) Cl and the OH groups are no more Lewis basic, but rather Brønsted acidic. Surface chlorination is in line with our previous XPS characterisation.⁸ H abstraction during dissociative HCl adsorption requires basic sites, and hence HCl adsorption is certainly retarded by the loss of basic character. Ammonia and CO adsorption studies by micro-calorimetry, FTIR, and TPD, confirmed the increase in the acidic character after Deacon reaction, at likely both the cus Ce⁴⁺ and OH positions. The calculated adsorption energies and vibrational frequencies by DFT were, generally, in accordance with the experiments. Due to the lack of other surface orientations considered and the partial sampling of potential defects, the DFT picture of CO and CO₂ adsorption and agreement to
experiment is far from perfect. However, the major changes in acid/base character are satisfactorily deduced.

Although HRTEM is not statistically conclusive, there is nevertheless an indication that the well-faceted surface of CeO₂ becomes rounded during the course of the reaction. The evolution of the OH band intensity at around 3730 cm⁻¹ may be related to this morphological modification of the surface. Nevertheless, no activation corresponding to the increase in OH density was observed with our CeO₂ catalyst, and therefore a direct correspondence between the overall OH intensity and the reactivity should be excluded.

The oxygen pressure dependence of HCl oxidation over CeO₂ shows a positive ~0.4–0.5 formal reaction order, even at high oxygen over-stoichiometry. Conversely, the effect of pHCl is positive (0.2–0.4) in high O₂ excess and gets negative for pHCl/pO₂ higher than ~1.5. This indicates that HCl activation is also an issue at low pHCl/pO₂, but O₂ activation is always difficult, essentially at all feed mixtures studied. Due to surface chlorination, low Cl coverage is likely not a factor for reactivity. Rather, if Cl coverage is high and/or Cl is too strongly bound, it blocks sites for elementary steps as HCl or O₂ activation.

The OH evolution in the pHCl and T dependent in situ FTIR experiment indicated that higher pO₂ and T will increase the OH density, and concomitantly the reaction rate increased. This might be interpreted as lowering surface Cl concentration by opening up sites capable of abstracting H from HCl and shifting equilibrium coverage toward higher OH density. On the other hand, even in those feed conditions, under which increasing pO₂ would give rise to rate enhancement, pHCl was shown to increase reactivity with a concomitant decrease of OH density. These apparently opposite observations may be reconciled assuming the importance of repulsive lateral interactions (e.g. for HCl adsorption) in decreasing the heat of adsorption of surface species and thereby facilitating recombination and product desorption.
An alternative explanation may be related to surface restructuring as a function of $p$HCl/$p$O$_2$, which if facile could allow two parameters (structure and coverage) to control reactivity. Despite the rapid changes in the OH density following the variation in the parameter field studied, the above results and discussion suggest that one cannot assign the OH concentration per se as the main descriptor of HCl oxidation reactivity. Further studies correlating surface OH and Cl concentration may clarify details in HCl oxidation over ceria not accessible from this work (Table 1).

Conclusions

Ceria is widely used as support, catalyst, or co-catalyst for various catalytic processes. We utilised ceria as the main active phase for the heterogeneous catalytic HCl oxidation. Here we compared the acid/base properties of bulk ceria in its fresh and post-reaction states by probe molecule adsorption (CO$_2$, NH$_3$, CO) applying micro-calorimetry, FTIR, TPD and DFT calculations. The results indicate that the basic character of the ceria surface has been essentially eliminated upon reaction in HCl oxidation. This can be explained with the replacement of surface lattice O with Cl species and that the OH groups formed are rather acidic in nature. An in situ FTIR reaction cell has been developed in order to follow the evolution of OH groups during HCl oxidation. OH groups are reaction intermediates in HCl oxidation. The effect of various catalytic processes. We utilised ceria as the main active parameter (structure and coverage) to control reactivity. Despite the rapid changes in the OH density following the variation in the parameter field studied, the above results and discussion suggest that one cannot assign the OH concentration per se as the main descriptor of HCl oxidation reactivity. Further studies correlating surface OH and Cl concentration may clarify details in HCl oxidation over ceria not accessible from this work (Table 1).

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Notes and references


