



Do observations on surface coverage-reactivity correlations always describe the true catalytic process? A case study on ceria

Ramzi Farra^a, Maik Eichelbaum^a, Robert Schlögl^a, László Szentmiklósi^b, Timm Schmidt^c, Amol P. Amrute^d, Cecilia Mondelli^d, Javier Pérez-Ramírez^d, Detre Teschner^{a,b,*}

^aFritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

^bCentre for Energy Research, Hungarian Academy of Sciences, Budapest H-1525, Hungary

^cBayer MaterialScience AG, PUR-PTI-PRI, Chempark B598, D-41538 Dormagen, Germany

^dInstitute for Chemical and Bioengineering, Department of Chemical and Applied Biosciences, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland

ARTICLE INFO

Article history:

Received 9 August 2012

Revised 27 September 2012

Accepted 28 September 2012

Available online 6 November 2012

Keywords:

CeO₂

In situ FTIR

In situ PGAA

EPR

HCl oxidation

Surface coverage

ABSTRACT

In situ (operando) investigations aim at establishing structure–function and/or coverage–reactivity correlations. Herein, we investigated the gas-phase HCl oxidation ($4\text{HCl} + \text{O}_2 \rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$) over ceria. Despite its remarkable performance, under low oxygen over-stoichiometry, this oxide is prone to a certain extent to subsurface/bulk chlorination, which leads to deactivation. *In situ* Prompt Gamma Activation Analysis (PGAA) studies evidenced that the chlorination rate is independent of the pre-chlorination degree but increases at lower oxygen over-stoichiometry, while dechlorination is effective in oxygen-rich feeds, and its rate is higher for a more extensively pre-chlorinated ceria. Even bulk CeCl₃ could be transformed into CeO₂ under oxygen excess. Electron Paramagnetic Resonance experiments strongly suggested that oxygen activation is inhibited by a high surface chlorination degree. The coverages of most abundant surface intermediates, OH and Cl, were monitored by *in situ* infrared spectroscopy and PGAA under various conditions. Higher temperature and $p(\text{O}_2)$ led to enhanced OH coverage, reduced Cl coverage, and increased reactivity. Variation of $p(\text{HCl})$ gave rise to opposite correlations, while raising $p(\text{Cl}_2)$ did not induce any measurable increase in the Cl coverage, despite the strong inhibition of the reaction rate. The results indicate that only a small fraction of surface sites is actively involved in the reaction, and most of the surface species probed in the *in situ* observation are spectators. Therefore, when performing *in situ* steady-state experiments, a large set of variables should be considered to obtain accurate conclusions.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

Heterogeneous catalysis is a kinetically driven phenomenon, and the reaction rate is proportional to the coverage of *at least one* reactant, or surface species or by the number of free sites. Nevertheless, the dependence can be fairly complex, and the extent of sites occupied by blocking species crucially affects the catalyst's efficiency. The coverage of reactants, intermediates, and products strongly depends on their heat of adsorption at the relevant active surface site and on the barriers related to the formation and elimination of these surface species. The quantitative information on the surface coverage plays an important role in identifying reaction mechanisms, designing alternative catalysts, or validating purely computational approaches. Thus, the knowledge of the surface coverage at meaningful catalytic turnover is critical and has motivated extensive

experimental efforts [1–3]. Unfortunately, only a very few number of experimental techniques are capable of deriving such information, the most important ones being the various forms of vibrational spectroscopies. In this manuscript, we will experimentally assess the coverage of surface species under catalytic turnover and correlate these with the reactivity. The catalytic HCl oxidation (Deacon reaction) over bulk ceria will serve as our example.

The heterogeneously catalyzed HCl oxidation is a sustainable route to manufacture chlorine, and the current technology is based on RuO₂ catalysts [4–8]. CeO₂ was recently identified as a cheaper potential alternative active phase in view of its remarkable stability, though it requires higher operating temperatures [9]. As revealed by XRD and XPS analyses, when using an appropriate over-stoichiometry of oxygen in the feed gas ($\text{O}_2:\text{HCl} > 0.75$), the bulk of ceria was unaffected, and only the surface got chlorinated under reaction condition. The mechanism of HCl oxidation over CeO₂ was suggested to involve the following elementary steps: (i) hydrogen abstraction from HCl by basic surface O atoms to form hydroxyl groups leaving chlorine atoms on the surface, (ii) reaction

* Corresponding author at: Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany. Fax: +49 30 84134676.

E-mail address: teschner@fhi-berlin.mpg.de (D. Teschner).

of the hydroxyl groups with new incoming HCl molecules and/or hydroxyl group recombination on the surface to form water, (iii) water desorption, (iv) reoxidation of the surface via dissociative adsorption of O₂, and (v) recombination of chlorine atoms evolving as gas-phase Cl₂ [9]. Several of these steps rely on the existence of anionic oxygen vacancies that accommodate dissociated reactants. Based on the above mechanism, adsorbed Cl, OH, and H₂O are the major species populating the surface. These may occupy coordinatively unsaturated cationic sites or lattice O sites by replacement.

This manuscript attempts to address two novel aspects of the Deacon reaction over CeO₂. First, we investigate the chlorine uptake under reaction conditions and follow the kinetics of the dynamic chlorination and dechlorination processes depending on the oxygen over-stoichiometry of the feed mixture. Second, we examine the coverage of Cl and OH under various reaction conditions and relate them with reactivity. We show how convincing coverage-rate correlations break down when product inhibition is included in the experiments and conclude that the observed correlations are associated with the main part of the surface bearing little relevance for the reactivity.

2. Experimental

2.1. Catalysts

CeCl₃ (Alfa Aesar, ultra dry, 99.9%) was used as received. CeO₂ (Aldrich, nanopowder, 544,841) was calcined in static air at 1173 K for 5 h prior to use. This sample is referred to as CeO₂-A. CeO₂-R was synthesized by thermal decomposition of cerium(III) nitrate hexahydrate (Aldrich, 99.99%) in air by ramping to 1173 K (2 K min⁻¹) and holding for 3 h. CeO₂-A and CeO₂-R possessed BET surface areas of 21 and 5 m² g⁻¹, respectively, after catalytic testing. For the EPR experiments, CeO₂-A was treated in O₂:HCl = 0.75 at 703 K for 3 h. This sample is denoted as CeO₂-D.

2.2. Basic characterization

Powder X-ray diffraction (XRD) was measured in a PANalytical X'Pert PRO-MPD diffractometer. Data were recorded in the 10–70° 2θ range with an angular step size of 0.017° and a counting time of 0.26 s per step. N₂ sorption at 77 K was measured in a Quantachrome Quadrasorb-SI gas adsorption analyzer. The samples were degassed in vacuum at 473 K for 12 h prior to the measurement.

2.3. In situ Prompt Gamma Activation Analysis (PGAA)

In situ PGAA [10] was utilized to measure the Cl uptake of ceria during HCl oxidation. The technique is based on the detection of element-specific gamma rays emitted upon the capture of neutrons by the nucleus. The investigated volume, in our case, a tubular micro-reactor (catalyst bed volume ~0.3 cm³), was probed, and the amounts of Cl and Ce were quantified. PGAA was carried out under atmospheric pressure condition at the cold neutron beam of the Budapest Neutron Centre. A Compton-suppressed high-purity germanium crystal was used to detect the prompt gamma photons. Molar ratios (Cl:Ce) were determined from the characteristic peak areas corrected by the detector efficiency and the nuclear data of the observed elements. The gas-phase Cl signal (HCl, Cl₂) was subtracted; thus, all Cl:Ce ratios reported here correspond only to the catalyst itself. The quartz reactor (8 mm i.d.) was placed into the neutron beam and surrounded by a specially designed oven having openings for the incoming and outgoing neutrons and for the emitted gamma rays toward the detector. These openings were covered by thin aluminum foils to minimize heat losses. Two ceria samples

(CeO₂-A, CeO₂-R) were investigated. As both revealed the same trends, only the more detailed investigation on CeO₂-R is presented in the PGAA section, while results on CeO₂-A are collected in the [Electronic supplementary information \(ESI\)](#). 0.8 g of CeO₂-R (sieve fraction 0.1–0.32 mm) was loaded into the reactor. The reaction feed, at a constant total flow of 166.6 cm³ STP min⁻¹, was supplied by mass flow controllers and employed HCl (4.5), O₂ (5.0), N₂ (5.0), and Cl₂ (4.0). Various feed compositions, *p*(O₂), *p*(HCl), and *p*(Cl₂), and reaction temperature were investigated. Details are provided at the appropriate sections. The Cl₂ production was monitored by iodometric titration. The percentage of HCl conversion was determined as $X_{\text{HCl}} = (2 \times \text{mole Cl}_2 \text{ at the reactor outlet} / \text{mole HCl at the reactor inlet}) \times 100$. Further details on the technique and representative spectra are provided in the ESI.

2.4. Catalytic evaluation

The gas-phase oxidation of hydrogen chloride was studied at ambient pressure in a set up described elsewhere [11]. The catalyst (sieve fraction = 0.4–0.6 mm) was loaded in the tubular reactor (8 mm i.d.) and pretreated in N₂ at 703 K for 30 min. Thereafter, the reaction gases were introduced at a total flow of 166 cm³ STP min⁻¹. CeCl₃ was tested at 703 K or 723 K, O₂:HCl = 2, 4, or 9, and a catalyst weight of 0.5 g. Separated 5 h tests were carried out with fresh loads of CeCl₃ for each O₂:HCl ratio and temperature. Used samples were collected for *postmortem* characterization after rapidly cooling down the reactor to room temperature in a flow of N₂. Activity data were collected for CeO₂-A after 1 h on stream under all conditions applied to CeCl₃ to serve as reference. The influence of Cl₂ co-feeding on the rate of HCl oxidation over CeO₂-A was studied by introducing fixed amounts (2, 3, 4, and 5 cm³ STP min⁻¹) of Cl₂ to the inlet feed at 703 K and O₂:HCl = 9 (notice HCl flow is 16.6 cm³ STP min⁻¹), over 0.25 g of catalyst. Data were taken after 1.5 h on stream under each condition. Cl₂ quantification and calculation of the HCl conversion were performed as described in the above section.

2.5. In situ Fourier Transform Infrared Spectroscopy (FTIR)

A specially designed homemade cell was used to investigate Deacon catalysts under reaction conditions [12]. For *in situ* FTIR experiments, 42 mg CeO₂-A was pressed into a self-supporting disk (31.8 mg cm⁻²). The sample was placed in the sample holder, which serves as an internal furnace as well. The pellet was pretreated *in situ* by heating it in synthetic air up to 723 K (10 K min⁻¹). Spectra were recorded with a Varian-670 FTIR spectrometer (resolution = 4 cm⁻¹). In most cases, 512 scans were averaged to achieve a satisfactory signal-to-noise ratio. Mass flow controllers were used to supply the reaction feed (total flow = 100 cm³ STP min⁻¹). The effect of *p*(O₂), *p*(HCl), and temperature was investigated under Deacon conditions. In the O₂ partial pressure-dependent series, the HCl flow was kept constant at 10 cm³ STP min⁻¹, and *p*(O₂) was varied to give the following feed composition sequence O₂:HCl:N₂ = 9:1:0, 4:1:5, 2:1:7, 1:1:8 and 0.5:1:8.5. During the measurement of the HCl partial pressure dependence, the O₂ flow was kept constant at 20 cm³ STP min⁻¹, and HCl flow was varied as follows: 10, 6, 3, and 1 cm³ STP min⁻¹. In the partial pressure variation experiments, the temperature was kept at 703 K. The temperature dependence was investigated by reducing the temperature stepwise, 20 K per step, between 703 and 623 K using a feed of O₂:HCl:N₂ = 9:1:0.

2.6. Electron Paramagnetic Resonance (EPR) experiments

The X-band EPR experiments were performed in vacuum (1 × 10⁻⁴–8 × 10⁻⁵ mbar) at 77 K on a Bruker ESP 300E

Download English Version:

<https://daneshyari.com/en/article/6527788>

Download Persian Version:

<https://daneshyari.com/article/6527788>

[Daneshyari.com](https://daneshyari.com)