Surface Chemistry

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Stable Deacon Process for HCl Oxidation over RuO_2**

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Industrial chemistry extensively employs chlorine as an oxidizing agent in a variety of organic processes. In the course of these processes hydrogen chloride is formed as an inevitable by-product either directly by substitution reaction or by subsequent production steps to obtain chlorine-free final products. Industrial uses exist for HCl, but chlorine processes produce much more of the by-product HCl than the market can absorb, resulting in a toxic-waste disposal problem. Consequently there has been growing interest in finding efficient methods for recycling chlorine from hydrogen chloride to design closed process cycles in industrial (chlorine-related) chemistry. However, all the known heterogeneously catalyzed processes for the oxidation of HCl with air to produce Cl_2 and water (Deacon process) have suffered, most notably, from the rapid loss of catalyst activity owing to catalyst instability. Therefore, the Deacon process has largely been displaced by electrolysis, a highly energy-consuming process.

Only recently, Sumitomo Chemicals[1] developed an efficient and stable reaction route for catalyzed HCl oxidation over ruthenium dioxide supported on rutile TiO_2 (Sumitomo process). The Sumitomo process is considered as a true breakthrough in the recovery of Cl_2 from HCl and a big step towards sustainable chemistry by reducing the unit energy consumption to only 15% of that required by the recently developed Bayer & Uhdenora electrolysis method.[2] Herein we show that the extraordinary stability of $RuO_2(110)$, a model catalyst for the Sumitomo process, is related to the selective replacement of bridging O atoms (O_{br}) at the catalyst surface by chlorine atoms (Figure 1).

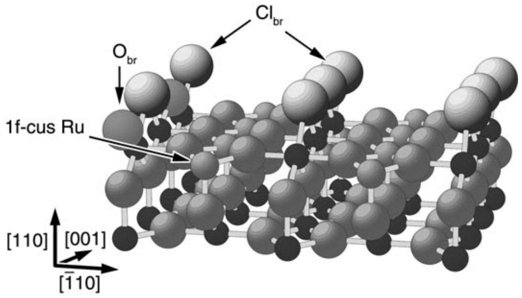

Figure 1. Ball-and-stick model showing the rutile structure of $RuO_2(110)$ with the undercoordinated surface atoms: bridging O atoms (O_{br}) and onefold coordinatively unsaturated Ru sites (1f-cus Ru). Upon HCl exposure at elevated temperatures part of the bridging O atoms are selectively replaced by bridging Cl atoms (Cl_{br}). This chlorinated surface is referred to as $RuO_{2-x}Cl_x(110)$.

In Figure 2 we present experimental high-resolution core-level shift (HRCLS) spectra[3] of O1s and Cl2p upon exposure of the $RuO_2(110)$ surface to 10 L HCl at 220 K and subsequent annealing to 420 K and 600 K. In the Cl2p spectra (Figure 2a), the two observed emission features are due to spin–orbit splitting ($Cl2p_{3/2}$, $Cl2p_{1/2}$). The Cl2p spectrum for HCl exposure at 220 K reveals relatively broad emission features which sharpen considerably after annealing the

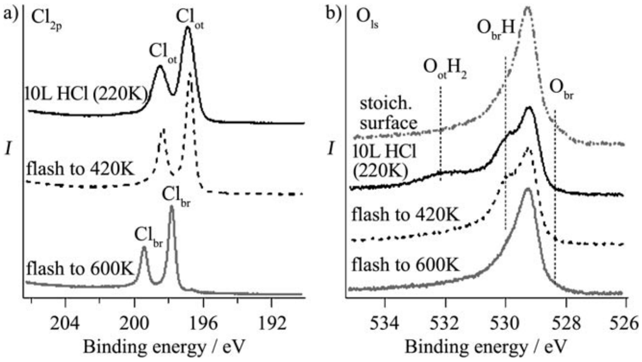

Figure 2. High-resolution core-level shift (HRCLS) spectra of Cl2p (a) and O1s (b) of the stoichiometric $RuO_2(110)$ surface in comparison with a $RuO_2(110)$ surface which is exposed to 10 L of HCl at 220 K and subsequently annealed to 420 K and 600 K. The assignment of particular core-level features to particular adsorption sites of Cl (Cl_{ot}, Cl_{br}) and O (O_{br}, $O_{br}H$, $O_{ot}H_2$) is based on DFT-calculated core-level shifts.

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surface to 420 K, the desorption temperature of water. Upon annealing to 420 K the integrated photoemission intensity declines by 15%, consistent with the corresponding thermal desorption spectrum (TDS) of HCl (see Figure S1 in the Supporting Information). Upon annealing the chlorinated surface to 600 K, the Cl2p components shift by 1.09 eV to higher binding energies and the emission intensity decreases further by 30%. From TDS data (Figure S1 in the Supporting Information) we know that only HCl desorbs and Cl_2 is not produced. DFT-calculated[4] Cl2p core-level shifts indicate that the experimentally observed Cl2p shift can be assigned to a change of the adsorption site of chlorine atoms from the on-top position above the 1f-cus Ru site (1f-cus stands for onefold coordinatively unsaturated site) towards the bridge position, replacing the O_{br} atoms with Cl_{br} atoms. (Figure 1) The DFT-calculated Cl2p shift is 1.37 eV, which is in good agreement with the HRCLS experiment (1.09 eV). Assuming that exposure to 10 L HCl at 220 K saturates the surface with one monolayer of HCl and neglecting diffraction effects, the integrated Cl2p signal in Figure 2a suggests a coverage of adsorbed Cl of half a monolayer after annealing the HCl saturated surface to 600 K.

Additional support for the replacement reaction of O_{br} by Cl comes from the O1s spectra in Figure 2b of the stoichiometric $RuO_2(110)$ surface in comparison with the HCl-treated surface. After exposing the $RuO_2(110)$ surface to 10 L of HCl at 220 K the O_{br} emission disappears and two additional components appear in the O1s spectrum at binding energies of 530 eV and 532 eV. From a previous study we know that the O1s emission at 530 eV is related to bridging hydroxy groups $O_{br}H$,[5] that is, the bridging O atoms are bonded by hydrogen atoms. The hydrogen atoms in the $O_{br}H$ groups originate from the hydrogen transfer from adsorbed HCl to the bridging O atoms, forming on-top Cl (Cl_{ot}) and bridging hydroxy groups. The other O1s emission feature at 532 eV is ascribed to adsorbed water on 1f-cus Ru sites.[5] Part of the $O_{br}H$ species react with additional hydrogen units, thereby forming water molecules ($O_{ot}H_2$) over the 1f-cus Ru atoms and vacancies in the O_{br} rows of the $RuO_2(110)$ surface. Below 420 K no on-top Cl atoms migrate into these bridging O vacancies, most probably owing to a high activation barrier for diffusion. Annealing the surface to 420 K leads to desorption of the on-top-adsorbed water species and the disappearance of the O1s component at 532 eV. This process is accompanied by a pronounced sharpening of the corresponding Cl2p photoemission spectra. Therefore, we propose that hydrogen bonding of water with Cl causes the pronounced broadening of the Cl2p features in Figure 2a. The O1s intensity of the $O_{br}H$ groups is not affected by annealing to 420 K (Figure S2 in the Supporting Information). Upon annealing to 600 K the $O_{br}H$-related O1s emission disappears and part of the O_{br} emission is recovered. This observation is reconciled with the process of $O_{br}H$ recombination to produce water (which desorbs immediately), thereby forming vacancies in the O_{br} rows and bare O_{br} species. At 600 K the vacancies in the O_{br} rows are filled by Cl atoms, as indicated by a shift of the Cl2p spectrum by 1.09 eV (Figure 2). Altogether, this experiment reveals nicely the selective replacement of O_{br} by Cl.

A third piece of evidence for the selective replacement of O_{br} by Cl is provided by a full structural analysis of the chlorinated $RuO_2(110)$ surface (referred to as $RuO_{2-x}Cl_x(110)$) by application of the standard surface crystallographic technique of low-energy electron diffraction (LEED).[6] The quality of the LEED pattern is identical before and after HCl exposure with annealing to 600 K, indicating that the morphology of the oxide surface has not deteriorated. For a quantitative LEED analysis we collected LEED intensity curves as a function of the kinetic energy of the incident electrons of the HCl-treated $RuO_2(110)$ surface and compared these experimental data with theoretical LEED data of a presumed model structure computed by a full dynamical LEED program code by using an automated optimization scheme for the structural refinement.[7] The LEED analysis of the chlorinated $RuO_2(110)$ surface showed that $50 \pm 20\%$ of the bridging O atoms are replaced by Cl atoms,[8] in agreement with the above interpretation of the HRCLS data.

The replacement of the bridging O atoms of $RuO_2(110)$ is also corroborated by CO redox reaction experiments. It is known that exposure of the stoichiometric $RuO_2(110)$ surface to CO and annealing to 600 K results in the formation of CO_2 by the recombination of on-top adsorbed CO molecules with bridging O atoms, thereby reducing the oxide surface.[9] If part of the bridging O atoms are replaced by Cl, then the conversion of CO into CO_2 should decrease. Indeed we observe in Figure 3 a substantial decrease of the CO oxidation yield when part of the bridging O atoms are replaced by Cl atoms as realized by exposure to 10 L HCl at 220 K and annealing to 600 K. By exposing the stoichiometric $RuO_2(110)$ surface to 20 L HCl at 700 K all bridging O atoms are replaced by Cl atoms, as confirmed by a quantitative LEED study.[8] Upon CO exposure and running a

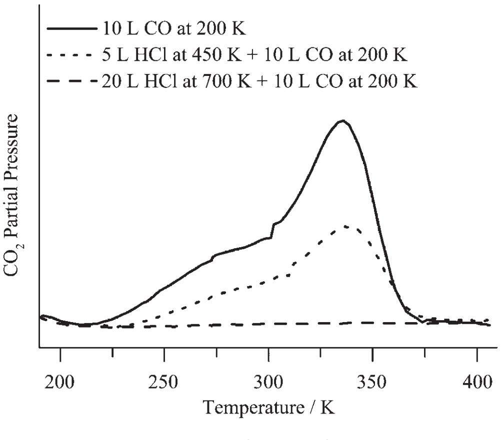

Figure 3. Temperature-programmed CO oxidation reaction experiments over the chlorinated $RuO_{2-x}Cl_x(110)$ surface in comparison with the stoichiometric $RuO_2(110)$ surface. The chlorinated $RuO_{2-x}Cl_x(110)$ surface was prepared either by exposure of 5 L HCl to $RuO_2(110)$ at 450 K or by exposure of 20 L HCl to $RuO_2(110)$ at 700 K. Finally, in all cases 10 L CO was exposed to the surface at 200 K. Since no oxygen is supplied from the gas phase, the CO_2 signal measures directly (i.e. titrates) the amount of bridging O atoms left on the catalyst surface after the HCl treatment. CO_2 partial pressure is shown in arbitrary units.

thermal desorption experiment up to 650 K, no CO_2 formation was observed, as indicated in Figure 3. Rather, all adsorbed CO desorbs from the surface.

The chlorinated $RuO_{2-x}Cl_x(110)$ surface is able to oxidize HCl to Cl_2 and water (Figure 4). Here we exposed the chlorinated $RuO_{2-x}Cl_x(110)$ surface to 0.1 L of oxygen and 1.3 L of HCl at 100 K and subsequently ran a temperature-programmed reaction experiment up to 800 K while monitoring water, Cl_2, and HCl with a mass spectrometer. HCl desorbs to some extent at about 500 K, Cl_2 is formed above 600 K, and the produced water desorbs around 420 K. This experiment shows nicely that the chlorinated $RuO_{2-x}Cl_x(110)$ surface catalyzes the HCl oxidation, thus validating $RuO_{2-x}Cl_x(110)$ as an appropriate model catalyst for the Sumitomo process. Similar results were also obtained for a $RuO_{2-x}Cl_x(110)$ surface on which all of the bridging O atoms are replaced by Cl atoms.

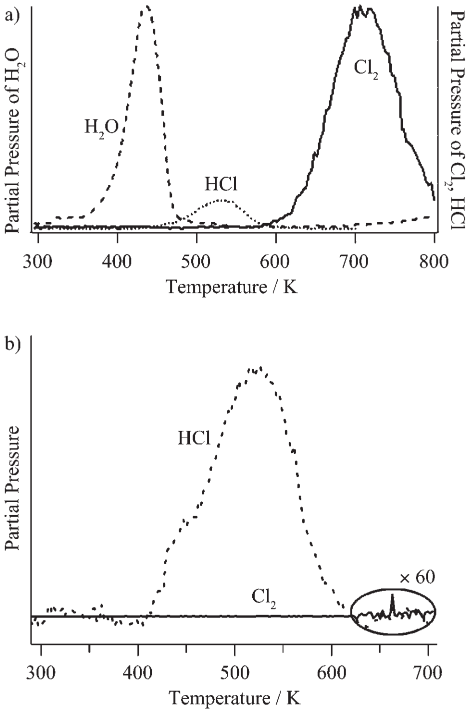

Figure 4. a) Thermal desorption and reaction experiment of the coadsorption of 0.1 L of O_2 and 1.3 L of HCl to a chlorinated $RuO_{2-x}Cl_x(110)$ surface on which most of the bridging O atoms have been replaced by chlorine atoms. Part of the HCl molecules desorb already around 500 K, while the rest of the adsorbed HCl molecules react with on-top O atoms to form the water and desired product Cl_2. b) Analogous experiment performed with no oxygen supply, leading only to the desorption of HCl but no Cl_2 production (in the relevant temperature range, the Cl_2 signal is magnified by a factor of 60). Partial pressures are shown in arbitrary units.

The bridging chlorine atoms of the $RuO_{2-x}Cl_x(110)$ surface are thermally stable up to 800 K, which is 50 K below the decomposition temperature of $RuO_2(110)$. A temperature of 800 K is compatible with DFT calculations, from which the Cl_{br}–Ru binding energy was determined to be 2.1 eV (compared to 2.36 eV for O_{br}–Ru). But even more importantly, the chlorinated $RuO_{2-x}Cl_x(110)$ surface is also chemically stable. Excessive oxygen exposures at 600 K were not sufficient to replace the substituted chlorine atoms from the bridge sites. The main reason why the Cl_{br} atoms are chemically less active than the O_{br} atoms is that O_{br} carries a dangling bond,[11] while Cl_{br} does not. As soon as all bridging positions are occupied by Cl atoms, further HCl exposure and annealing to 750 K does not lead to Cl_2 formation, that is, no further oxygen of $RuO_2(110)$ is consumed (Figure 4b). This experiment shows that the chlorination process is *self-limiting*, an observation which is decisive for the observed stability of RuO_2 in the Sumitomo process. Altogether, the chlorinated $RuO_{2-x}Cl_x(110)$ catalyst is chemically stable under typical Deacon-type reaction conditions, neither reducing RuO_2 to metallic ruthenium nor transforming it to a pure ruthenium chloride compound.

A comparison of the chemical stability of the chlorinated $RuO_{2-x}Cl_x(110)$ surface with that of the stoichiometric $RuO_2(110)$ surface underscores the particular role of the bridging chlorine atoms in stabilizing the $RuO_2(110)$ surface. $RuO_2(110)$ can be easily reduced to metallic Ru when reducing agents such as hydrogen, CO, and methanol are applied at 420 K.[12,13] In other words, the $RuO_2(110)$ catalyst is not stable under such strongly reducing reaction conditions. The reduction process of $RuO_2(110)$ starts with the removal of bridging O atoms from the RuO_2 surface by the reducing agent. Subsequently, the created bridging O vacancies are filled by the diffusion of bulk-coordinated surface oxygen of RuO_2 into these vacancies. This process produces highly undercoordinated Ru atoms at the surface which agglomerate into small Ru islands. With STM the reduction mechanism has been studied on the microscopic scale.[14]

HCl is an equally strongly reducing agent as CO and H_2. However, the full reduction of $RuO_2(110)$ is prevented by the stabilization of the oxide surface through the selective replacement of bridging O atoms by Cl atoms. This replacement process suppresses the migration of bulk-coordinated oxygen atoms into the bridging positions and therefore the progressing reduction of RuO_2 towards Ru.

In conclusion, the $RuO_2(110)$ surface is chlorinated during the catalyzed oxidation of HCl with oxygen by selective replacement of bridging O atoms by bridging Cl atoms. The chlorination process of $RuO_2(110)$ is self-limiting in that chlorine incorporation terminates when all bridging O atoms are replaced by Cl atoms. The $RuO_{2-x}Cl_x(110)$ surface is active and stable in the oxidation of HCl to Cl_2 and water, thus serving as an appropriate model catalyst for the Sumitomo process.

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