Heterogeneous Catalysis

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The Electronic Factor in Alkane Oxidation Catalysis**

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Abstract: *This article addresses the fundamental question of whether concepts from semiconductor physics can be applied to describe the working mode of heterogeneous oxidation catalysts and whether they can be even used to discriminate between selective and unselective reaction pathways. Near-ambient-pressure X-ray photoelectron spectroscopy was applied to the oxidation of n-butane to maleic anhydride on the highly selective catalyst vanadyl pyrophosphate and the moderately selective MoVTeNbO$_x$ M1 phase. The catalysts were found to act like semiconducting gas sensors with a dynamic charge transfer between the bulk and the surface, as indicated by the gas-phase-dependent response of the work function, electron affinity, and the surface potential barrier. In contrast, only a minor influence of the gas phase on the semiconducting properties and hence no dynamic surface potential barrier was monitored for the total oxidation catalyst V$_2$O$_5$. The surface potential barrier is hence suggested as descriptor for selective catalysts.*

Since the middle of the last century, semiconductor physics concepts have been used to explain the working mode of selective alkane and alkene oxidation catalysts.[1–7] The vision was—and still is—to predict the catalytic activity and selectivity of materials in different reactions on the basis of their electronic structure (the so-called "electronic factor"). In semiconductor theory the difference between the Fermi potential of the semiconducting catalyst and the redox potential of adsorbates creates a driving force for charge transfer across the bulk–surface–adsorbate interface.[5,8] This charge transfer generates a potential gradient and hence electric field between surface and bulk and can induce conductive channels with current-rectifying properties like in a p–n junction diode.[9] The height of this surface potential barrier, which charge carriers have to overcome to move between bulk and surface, could have a significant kinetic impact on the oxidation reaction on the surface and the activation of oxygen.[5] The surface barrier height under steady-state reaction conditions could hence be a descriptor for the catalytic performance of oxidation catalysts. However, it has not yet been proven that oxidation catalysts act indeed like semiconducting gas sensors with the formation of a surface potential barrier controlled by the gas phase.

Understanding the working mode of vanadyl pyrophosphate (VPP), which is the commercial catalyst for the oxidation of *n*-butane to maleic anhydride,[10–14] is of general interest, since it is a benchmark system in selective oxidation catalysis,[15–21] representing one of the most important class of heterogeneously catalyzed reactions in the context of the anticipated paradigm shift in raw materials.[22] Due to its increasing conductivity in air and decreasing conductivity in *n*-butane-containing gas mixtures, VPP was identified as a p-type semiconductor with electron holes as the majority charge carriers.[10–14,23–25] However, the gas-phase-dependent conductivity response alone is not a sufficient descriptor for selectivity, since vanadium(V) oxide exhibits a reversible conductivity response under reaction conditions[26] but catalyzes only the total oxidation of *n*-butane to CO and CO$_2$.

Herein we report on the successful application of near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS) to investigate the influence of the reactive gas phase on the surface potential barrier of VPP under catalytic *n*-butane oxidation conditions with proven production of maleic anhydride. The results show that the transfer of charge carriers between the bulk catalyst and the surface can be explained by—and are thus the first experimental proof for—the previously only theoretically proposed semiconductor catalyst concepts of Boudart,[1] Schwab,[2] Volkenshtein,[3] and Morrison.[4,5] We compare these results with the electronic response of the unselective oxidation catalyst V$_2$O$_5$ and the moderately selective catalyst MoVTeNbO$_x$ (orthorhombic M1 phase) in order to identify a general concept that can explain selectivity.

We investigated the polycrystalline catalyst VPP with NAP-XPS at 25 Pa and 400 °C in 1:10 mixtures of *n*-butane/oxygen (C$_4$H$_{10}$/O$_2$), helium/oxygen (O$_2$), and *n*-butane/helium (C$_4$H$_{10}$), according to the protocol described in the Supporting Information. The studied catalyst produces, in a fixed-bed flow-through reactor at 1 bar, maleic anhydride with a selectivity between 70 and 80 %.[24] In semiconductor physics,

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a gas-phas-dependent surface potential barrier (band bending) and hence a charge-carrier exchange between bulk and surface can be evidenced, if the work function, the valence band, and all core level binding energies are consistently shifted by the same absolute value upon adsorbing different gases (cf. Figure S2 in the Supporting Information).[8] Thus, we measured the dependence of the valence band onset, V 3d valence state, work function (by measuring the secondary electron cutoff), and the O 1s, V 2p, and P 2p core levels on the different gas mixtures. Figure 1 shows X-ray photoelectron (XP) spectra at high (secondary electron cutoff) and low binding energies (valence band) in the three different gas atmospheres. The peak close to the valence band at about 2–2.5 eV below the Fermi level (0 eV) is assigned to an occupied vanadium 3d state. Upon changing the applied gas mixture, the secondary electron cutoff, valence band onset, and V 3d state shift to higher binding energies under reducing C_4H_{10} conditions, while only slight differences can be recognized between spectra recorded in C_4H_{10}/O_2 and O_2 (Figure 1). Moreover, the peak intensity of the V 3d state increases under C_4H_{10} conditions, indicating a larger electron occupation of this valence state and hence reduction of the catalyst phase.

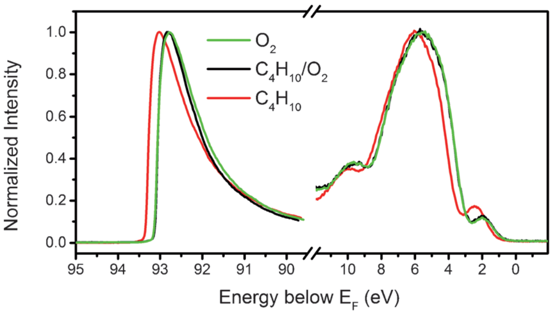

Figure 1. In situ XP spectra at the high (secondary electron cutoff; left) and low binding energy regions (valence band with V 3d state at about 2 eV; right) of VPP at 400 °C under catalytic working (C_4H_{10}/O_2), oxidizing (O_2), and reducing conditions (C_4H_{10}), respectively. The spectra were measured with an excitation energy of 100 eV.

Figure 2 summarizes the observed changes of the work function, V 3d state, vanadium oxidation state (deduced from the V $2p_{3/2}$ core level), and electron affinity. The binding energy shifts of the core levels V $2p_{3/2}$, O 1s, and P 2p are depicted in Figure S1 (Supporting Information). The V 3d state is reversibly shifted by up to 540 meV, while the measured core levels are reversibly shifted by about 500 meV between oxidizing O_2 and reducing C_4H_{10} conditions. This consistent behavior is a strong indication for a bulk–surface charge transfer accompanied by the formation of a subsurface space charge region and a gas-phase-dependent surface potential barrier (i.e. band bending). The proton-transfer reaction mass spectrometry (PTR-MS) signal at m/z 99 (mass of protonated maleic anhydride), recorded during the applied experimental protocol, proves that under C_4H_{10}/O_2 reaction conditions maleic anhydride is produced and that the catalyst was indeed studied under catalytic operation conditions (Figure 2 a).

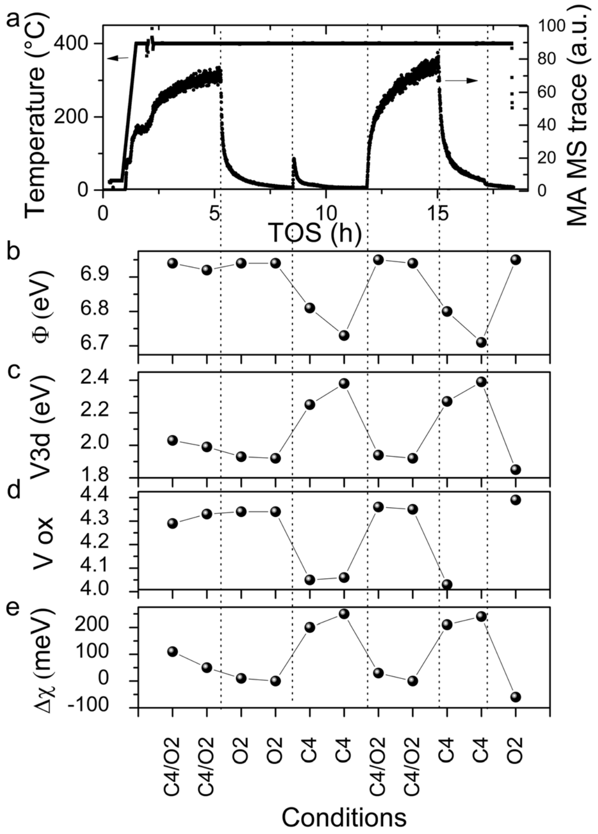

Figure 2. a) PTR-MS trace of maleic anhydride (MA; protonated mass 99) during time on stream (TOS) under the conditions indicated in the abscissa of (e); plots of b) work function Φ, c) V 3d valence state binding energy, d) average vanadium oxidation state (V ox) as deduced from the V $2p_{3/2}$ spectra, and e) electron affinity change $\Delta\chi$ ($\Delta\Phi-\Delta$BE-(V 3d), difference to second O_2 condition) of VPP at 400 °C in different gas mixtures.

The work function Φ is deduced by calculating the difference between the excitation energy and the energy value at half-maximum of the secondary electron cutoff. The measured work functions for VPP range between 6.94 eV in O_2 and 6.7 eV in C_4H_{10} (Figure 2 b). These values are comparable with the work function of the binary oxide V_2O_5 ($\Phi = 7.0$ eV).[27] As mentioned earlier, a pure Fermi level pinning to the adsorbate-induced surface states energy can be evidenced, if the work function and all valence and core level binding energies are consistently shifted by the same absolute value upon adsorbing different gases. However, the total changes of Φ are with up to 240 meV significantly smaller than that observed for the valence and core levels. Adsorbates on a surface of a semiconductor can not only induce surface states causing band bending, but they can also affect the surface dipolar structure,[8] which would be indicated by a modified surface electron affinity (Figure S2 in the Supporting Information). Since the energy shifts in the different gas mixtures between work function and valence/core level binding energies are different, the adsorbates have modified both surface dipoles and surface states.[8] Thus, this energy shift difference can be used to calculate the electron affinity change $\Delta\chi$ induced by the adsorbates (Figure 2 e). Moreover, the average vanadium oxidation state is with nearly 4.4 highest in O_2, and with 4.0 lowest in C_4H_{10} (Figure 2d). Since the core level spectra were measured at a kinetic energy corresponding to a mean free electron path of 0.7 nm and hence pertain basically to the very first surface layer(s), the surface of VPP is obviously oxidized under O_2 and C_4H_{10}/O_2 conditions in comparison to the VPP bulk vanadium oxidation state of 4.0.

The obtained results for the electronic response of VPP in the different gas mixtures are schematically summarized in a simplified band diagram (Figure 3). Notably, the electronic structure of the catalyst does not have to be necessarily described by delocalized bands. If Fermi–Dirac electron statistics can be applied and electron or electron hole conduction can be described by a hopping mechanism of charge carriers between localized molecular orbitals, a similar electrochemical double-layer with an electric field between surface and bulk will form and similar binding energy shifts of the valence and core levels can be expected.

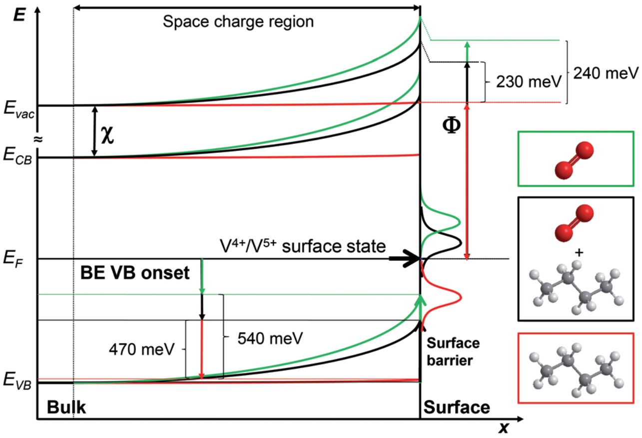

Figure 3. Schematic band diagram of VPP with experimentally obtained values for the binding energy (BE) shifts of the valence band (VB) onset and of the work function Φ measured in *n*-butane/helium (red), *n*-butane/oxygen (black), oxygen/helium (green). E_{VB}: valence band onset, E_F: Fermi level, E_{CB}: conduction band minimum, E_{vac}: vacuum level, χ: electron affinity.

Band bending and the surface potential barrier are induced by the pinning of the Fermi potential to the surface state potential, which in turn is modified by the chemical potential of the gas phase. The surface states could be identified by a V^{4+}/V^{5+} redox couple on the surface. In this case, the Fermi level (E_F) pinning is given by Equation (1).[5]

$$E_F(\text{with surface states}) = E_t + kT \ln \frac{[V^{4+}]}{[V^{5+}]} \tag{1}$$

E_t could be approximated by the redox energy of the V^{4+}/V^{5+} couple. The suggested relationship between surface barrier (band bending) and vanadium oxidation state is strongly supported by the simultaneously observed modulation of the average vanadium oxidation state (Figure 2d) and intensity of the V 3d valence state (Figure 1). The surface potential barrier height qV_B is the difference between the (hypothetical) Fermi level of the catalyst without surface states and the Fermi level of the catalyst with surface states modified by the gas phase as defined in Equation (2).

$$qV_B = E_F(\text{without surface states, flatband}) - E_F(\text{with surface states}) \tag{2}$$

Many recent surface-sensitive experiments under reaction conditions indicate that the catalyst is terminated by a two-dimensional vanadium(IV,V) oxide layer deviating significantly from the bulk crystal structure.[24,28–30] Hence, the proposed V^{4+}/V^{5+} surface states should be a part of this termination layer, or in the terminology of semiconductor physics,[5] they are extrinsic surface states from a surface termination with broken translational symmetry, as has been already suggested by Boudart with his concept of a "defect one-phase surface system".[1]

As indicated by Equations (1) and (2), a high V^{5+}/V^{4+} ratio can increase the surface barrier height qV_B to such an extent, that the bulk–surface electron transport is impeded. Under such conditions, also the activation (reduction) of gas-phase oxygen is strongly limited. As a consequence, the surface barrier confines the concentration of activated oxygen on the surface. Since an accumulation of oxygen will cause the total oxidation of the desired oxygenate to CO_x, the surface potential barrier could control the catalytic selectivity.

In order to check the suggested relationship between surface barrier and selectivity, the unselective (i.e. without selectivity to maleic anhydride, but only to CO and CO_2) catalyst vanadium(V) oxide was investigated by NAP-XPS. Under strongly oxidizing conditions in O_2 a maximum work function of 7.00 eV and a vanadium oxidation state of 4.9 is measured (Figure 4a). A reduction to an average vanadium oxidation state of 4.8 is observed in C_4H_{10} (Figure 4a). However, the work function is at the same time only slightly reduced to 6.96 eV. Moreover, the valence band onset is only weakly changed from 2.18 eV (O_2) to 2.22 eV (C_4H_{10}). Although all of these changes are reversible and hence real, they are much less pronounced than in VPP. As a consequence, the effect of the gases on the surface barrier is small. This can be explained by the much higher conductivity of V_2O_5,[26] where the depletion of electrons in the bulk by charge transfer between catalyst and gas phase is negligible compared to its high charge carrier density. Hence, the surface potential barrier due to a charge depletion in the subsurface space charge region is not modified further by the gas phase. This might have the consequence that the oxygen activation is not limited by the surface barrier, which could indeed explain the observed total oxidation of *n*-butane to CO_x.

In addition, we investigated an alternative selective *n*-butane oxidation catalyst, the orthorhombic $MoVTeNbO_x$ M1 phase, with a maleic anhydride selectivity of more than 40 %.[31] The conditions were shifted to 1:2 mixtures of ethane/O_2 and *n*-butane/O_2 to mimic a more oxidizing and reducing atmosphere, respectively, since the catalyst is not stable in pure O_2 or *n*-butane at reduced pressures. The vanadium oxidation state changed (reversibly) from about 4.6 to 4.5 (oxidation states of the other metal ions remained constant);[31] the work function shifted by 200 meV and the valence band onset by about 70 meV (Figure 4b), indicating

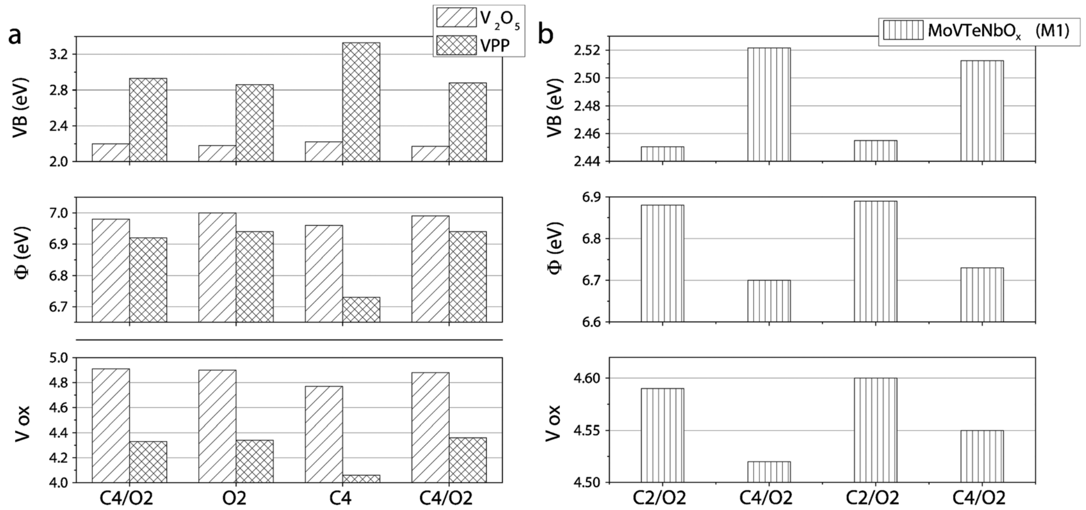

Figure 4. Valence band onset (VB), work function *Φ*, and surface vanadium oxidation state (V ox) of VPP, V_2O_5 (a) and $MoVTeNbO_x$ M1 phase (b) at 400 °C in different gas mixtures.

a gas-phase-dependent surface potential barrier and a change of the surface electron affinity by about 130 meV. Since the shifts are significantly larger than observed for V_2O_5, despite the more moderate changes in the oxidation/reduction conditions, these results are in line with the intermediate selectivity of this catalyst and support the concept of a surface-barrier-mediated bulk–surface charge transfer influencing the catalytic selectivity. The strong surface restructuring indicated by the change in electron affinity observed for both selective catalysts is in line with the idea that the active surface is formed in the presence of reaction gases, as generally observed in selective alkane oxidation catalysis.[32]

In conclusion, NAP-XPS experiments prove that the selective alkane oxidation catalysts VPP and $MoVTeNbO_x$ (M1 phase) act like semiconducting gas sensors with a gas-phase-dependent surface potential barrier. These results can hence be considered as experimental proof for the early semiconductor catalyst concepts of Boudart,[1] Schwab,[2] and Volkenshtein.[3] The formation of a dynamic surface potential barrier could give a rational description of catalytic selectivity under oxidation reactions. Within this concept the surface barrier controls the transfer of charge carriers between bulk and surface, and hence the activation of oxygen on the surface. This interpretation is strongly supported by experiments on the unselective catalyst V_2O_5, where the effect of the gas phase on the surface potential barrier was minimal.

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