Oxygen activation

Adsorption, Activation and Dissociation of Oxygen on Doped Oxides

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Activation of small molecules is one of the key issues in heterogeneous catalysis.¹ Common diatomic species, such as O₂, H₂ and N₂, are chemically inert and require activation at elevated temperature and pressure. The associated barriers can be lowered with catalytically active metals that alter the stability of the molecules via electron-transfer into their anti-bonding orbitals. Also reducible oxides offer suitable sites for molecular activation, such as surface O vacancies.² Wide-gap materials, on the other hand, are unable to bind small molecules due to a high degree of surface saturation. Molecular activation can still be achieved if dopants are introduced into the host lattice.³ Low-valence impurities give rise to a reduced formation energy of O-vacancies,4,5 which in turn promote the binding of molecular species.^{6,7,8,9} Conversely, electron transfer from high-valence dopants directly prompts the adsorbates into an activated state.¹⁰ Against common perception, molecular activation on doped oxides does not require any structural defects, a condition that renders this mechanism interesting for high temperature applications in which surface irregularities typical heal out at short time scales. One model reaction, in which dopants may play a pivotal role for the molecular activation is the oxidative coupling of methane as it runs at temperatures above 1000 K only.11,12

The strong effect of donor-type impurities was recently shown for Mo-doped CaO films.¹³ After gold deposition at room temperature, only monolayer islands were observed on the surface. This unusual growth behavior was attributed to a charge transfer from the Mo dopants to the ad-gold, giving rise to a substantial increase of the metal-oxide adhesion.¹⁴ In this paper we show that dopantinduced charge-transfer is relevant also for the adsorption and activation of small molecules, such as O₂. Using scanning tunnel microscopy (STM) and density functional theory (DFT), we provide evidence that strongly bound O_2^- species with high susceptibility for dissociation form even on chemically inert CaO(001) after doping with Mo ions.

Figure 1 displays STM images of atomically flat, doped

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CaO(001) films before and after exposure to O₂. In empty-state images, the ad-species appear as circular depressions 0.6 Å in depth and 10 Å in diameter. Exposing them to electrons from the STM tip proves their molecular nature, as the adsorbates split into pairs of identical minima that are assigned to the respective O atoms (Fig. 2).¹⁵ Whereas a mean O-O distance of 10-15 Å is observed directly after dissociation, this number increases with time due to the repulsive character of the O-O interaction on the surface. The two types of oxygen can be distinguished also via their bias-dependent topographic appearance in the STM (Fig. 2c). While the molecules show pronounced negative contrast, the atomic species appear fainter and are surrounded by a sombrero ring.



Figure 1. STM images of **(a)** a pristine 25 ML CaO(001) film (4.0 V, $80 \times 80 \text{ nm}^2$) and **(b)** films after O₂ exposure of 5 L @ 20 K and **(c)** 200 L @ 300 K (40 × 40 nm²).



Figure 2. STM images of the same O₂-covered region of Mo-doped CaO taken (a) before and (b) after multiple scans at 4.0 V (3.3 V, 40 \times 40 nm²). Note the dissociation of most molecules into atom pairs upon electron injection from the tip. (c) Height profile and biasdependent contrast of oxygen molecules and atoms. While atoms appear with pronounced sombrero shapes at higher bias, the molecules are imaged as deep depressions in the surface.

The adsorption efficiency of oxygen strongly depends on the preparation history of the CaO films, in particular on the concentration of the Mo dopants. This becomes evident in Fig.3, which displays weakly and strongly doped CaO films after exposure to 5 L O2 at 20 K. Whereas Mo-poor films are unable to bind oxygen, an adsorbate concentration of ~1017 m-2 is revealed for Mo-rich preparations, indicating a crucial role of the dopants for binding. To correlate the Mo concentration with the CaO reactivity towards oxygen, we use the position the oxide conduction band with respect to the Fermi level as descriptor. With increasing donor concentration in the matrix, the band position experiences a downshift, as electrons are transferred from interfacial Mo species to the metal substrate below.¹⁶ This charge flow generates a positive interface dipole between oxide film and metal support that shifts the vacuum level and, closely related, the oxide conduction band to lower energy (Fig. 3b).



Figure 3. (a,c) STM images of strongly and weakly-doped CaO films after exposure to 5 L O_2 @ 20 K (40 × 40 nm²). The O_2 adsorption probability correlates with the position of the CaO conduction band, as measured with dl/dV spectroscopy (b). Step edges are preferred O_2 binding sites only on weakly doped films (see arrows in c).

We now observe a steep onset in the O_2 adsorption probability when the band edge drops below 3.0 eV, while films with a band position higher than 4.0 eV are unable to bind oxygen. Again, electron donation of the Mo impurities seems to be the crucial requirement for molecular activation.

Although the band edge is a non-local parameter, we believe that dopants and O_2 molecules interact directly with each other and not via a delocalized charge background. Experimental evidence comes from O_2 desorption experiments, in which isolated molecules are removed from the surface via a bias pulse with the tip (Fig. 4). In 50% of these experiments, a Mo donor becomes detectable below the molecule. Interestingly, the dopant never occupies a position directly in the top layer but sits in sub-surface oxide planes, as deduced from the diameter of characteristic charging rings emerging in the STM images (see Suppl. Information and Ref. 17 for details).

We conclude that the Mo ions are able to exchange charges with the surface O_2 even over larger distances, e.g. via electron tunneling being active over at least 1 nm.

The formation of superoxo (O_2^-) species on the surface of Modoped CaO is corroborated by spectroscopic techniques. In XPS, we find a downward shift of Ca(2p) and O(1s) binding energies by ~0.2 eV after dosing O₂ onto the films. The same trend is revealed for the band positions determined with STM conductance spectroscopy (see Supporting Information). Both shifts indicate a workfunc-

tion increase $\Delta \phi$ due to the electron transfer into the adsorbates. The amount of charge transfer can be quantified directly by measuring $\Delta \phi$ after desorbing the O_2^- species from a given surface region and monitoring the associated shift of the vacuum levels with STM spectroscopy (Fig. 4b).¹⁸ We find a rigid downshift of all states by 0.35 eV (workfunction reduction), being explained with the removal of vertical Mo^{s+}-O₂^s dipoles upon oxygen desorption. The Helmholtz formula $\Delta \varphi = \frac{e}{\varepsilon_0 \varepsilon_{Ca0}} \mu_{ad} N_{ad}$ allows us to connect this μ_{ad} value with the dipole strength μ_{ad} of the charge-transfer pairs. For an O₂ surface density of $N_{ad} = 10^{17} m^{-2}$ and a dielectric constant of $\varepsilon_{CaO} = 10$, we calculate a dipole moment of 3×10^{-28} C·m, which is compatible with transferring one electron from a Mo ion in the 6th subsurface plane into a surface O_2 . The last hint for O_2^- formation on doped CaO films comes from the facile dissociation of the molecules, which proceeds with ~100% probability when injecting 4.0 V electrons from the tip (1min @ 20 pA). The bond cleavage occurs as another electron enters the anti-bonding states of the already weakened superoxo species.



Figure 4. (a,c) Identical CaO region before and after O₂ desorption with the tip (3.3 V, $27 \times 27 \text{ nm}^2$). The inset shows a selected area with higher resolution, revealing characteristic ring structures below the O₂ molecules (see arrows). These rings are the charging finger-prints of Mo dopants in a near surface region (4.0 V, $17 \times 17 \text{ nm}^2$).¹⁷ (b) STM conductance spectra showing the downshift of CaO vacuum states after O₂ desorption from the surface.

The electron transfer between Mo donors and O₂ acceptors has been reproduced with DFT calculations performed at the B3LYP+ Dispersion level. On non-doped CaO(001), a neutral O2 molecule binds with 13 kJ/mol (mostly from dispersion forces) to a Ca-Ca bridge position, while Ca²⁺ top sites are less preferred. In contrast, an O_2^- species binds to the same bridge site with 87 kJ/mol when a Mo³⁺ ion is present in the third subsurface plane. The charge transfer into oxygen becomes even more favourable for Mo²⁺ donors in the oxide film, given their low ionization energy.¹³ Further evidence for the superoxo formation comes from the bond elongation (121 to 133 pm) and the reduced stretching frequency (1537 to 1200 cm⁻¹) computed for O₂ molecules on the doped oxide. Moreover, the total spin of the system decreases from $\frac{5}{2}(\frac{3}{2} \text{ for Mo}^{3+}(d^3))$ plus $^{2}/_{2}$ for O₂) to $^{3}/_{2}$ ($^{2}/_{2}$ for Mo⁴⁺(d²) plus $^{1}/_{2}$ for O₂⁻) in response to the charge transfer. And finally, we calculated a lower apparent dissociation barrier for superoxo species on doped (66 kJ/mol) compared to neutral O2 on pristine CaO (110 kJ/mol), following the trend observed experimentally. Further details on the nature of the superoxo species can be found in the Supplementary Information.

In summary, we have shown that O_2 molecules may be activated to form superoxo species even on smooth, defect-free surfaces of non-reducible oxides when dopants are present in the bulk. The O_2^-

is bound with ~100 kJ/mol, hence stable at room temperature, and prone to dissociation into atomic oxygen on the doped surface. We conclude that dopants may play a pivotal role in the activation of hydrocarbons on wide-gap oxides, and refer to a corresponding paper from the Schlögl group in this issue that demonstrates an unusually high reaction yield of a Fe-doped MgO powder sample in the oxidative coupling of methane.¹²

Experimental Section

CaO films are grown on Mo(001) via reactive Ca deposition in 5×10^{-7} mbar O₂ and annealing to 1000 K in vacuum. The films are characterized by a square (1×1) LEED pattern, indicative for the (001) termination of CaO, and flat terraces of ~100 nm² size in STM.¹⁹ The CaO films are subject to self-doping, proceeding via spontaneous diffusion of Mo ions from the metal support into the film at elevated temperature.²⁰ While interfacial oxide planes contain up to 25% of Mo ions, this number decreases with increasing film thickness. A desired Mo concentration in a near-surface region of the film can now be installed by varying thickness and annealing temperature, the latter promoting Mo diffusion. The Mo concentration is estimated from XPS, the number of near-surface impurities in STM images or, alternatively, the position of the CaO conduction band as deduced from STM conductance spectroscopy.

Computational Approach

The DFT calculations are performed with PBE²¹ and B3LYP²² exchange-correlation functionals and a TZVP basis set.²³ The Mo core electrons are described by the Hay-Wadt effective core potential.²⁴ Dispersion is added as a damped summation over 1/r⁶ atomatom terms using the Grimme parameterization.²⁵ We use Ca₃₄O₃₄ cluster models, surrounded by a shell of full-ion effective core potentials on Ca²⁺ positions and embedded into a periodic array of point charges.²⁶

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