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Energy Level Shifts at the Silica/Ru(0001) Heterojunction Driven by Surface and Interface Dipoles

Mengen Wang^{1,2} · Jian-Qiang Zhong¹ · John Kestell¹ · Iradwikanari Waluyo³ · Dario J. Stacchiola¹ · J. Anibal Boscoboinik¹ · Deyu Lu¹

Abstract Charge redistribution at heterogeneous interfaces is a fundamental aspect of surface chemistry. Manipulating the amount of charges and the magnitude of dipole moments at the interface in a controlled way has attracted tremendous attention for its potential to modify the activity of heterogeneous catalysts in catalyst design. Two-dimensional ultrathin silica films with well-defined atomic structures have been recently synthesized and proposed as model systems for heterogeneous catalysts studies. R. Włodarczyk et al. (Phys. Rev. B, 85, 085403 (2012)) have demonstrated that the electronic structure of silica/Ru(0001) can be reversibly tuned by changing the amount of interfacial chemisorbed oxygen. Here we carried out systematic investigations to understand the underlying mechanism through which the electronic structure at the silica/Ru(0001) interface can be tuned. As corroborated by both in situ X-ray photoelectron spectroscopy and density functional theory calculations, the observed interface

energy level alignments strongly depend on the surface and interfacial charge transfer induced dipoles at the silica/Ru(0001) heterojunction. These observations may help to understand variations in catalytic performance of the model system from the viewpoint of the electronic properties at the confined space between the silica bilayer and the Ru(0001) surface. The same behavior is observed for the aluminosilicate bilayer, which has been previously proposed as a model system for zeolites.

1 Introduction

Two-dimensional ultrathin silica films with well-defined atomic structures have recently attracted widespread interest due to their capabilities in modeling and understanding the structure–reactivity relationships in heterogeneous catalysts based on SiO₂, either as a support for metal catalysts [1, 2], or as part of the active structure [3], such as the case of zeolites [4]. In the past decade, intensive research efforts have been devoted to the preparation of well-ordered crystalline silica films on diverse metals, such as Mo(112), Ni(111), Pd(100), Pt(111), and Ru(0001) [5–10]. In particular, free-standing silica and aluminosilicate bilayer films with corner-sharing tetrahedra (TO₄, with T = Si or Al) have been successfully grown on noble metal substrates, in which the bilayer films interact weakly with the support via van der Waals (vdW) forces [9, 10]. The relatively weak interaction between the metallic substrate and the ultrathin (alumino) silicate film makes it possible to explore the fundamental aspects of the catalytic activity and selectivity by using these model systems [4]. Moreover, small molecules can intercalate and react at the interface [11–13], which provides a new playground to

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study chemical reactions at confined spaces using surface science methods [12]. Another important feature about this system, arising from the weak interactions between their components, is that the distance between the silica bilayer and the Ru(0001) surface can be tuned by the type and concentration of adsorbed molecules on the Ru(0001) surface [14].

Recently, the electronic properties involved in heterogeneous oxidation catalysts have been explored by M. Eichelbaum et al. in situ using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) [15]. It has been shown that a dynamic surface potential barrier can be used as a rational descriptor of catalytic selectivity under oxidation reactions [15]. Notwithstanding the great interest on the effect of interfacial electronic structures on catalytic performance, the origin of the dynamic surface potential barrier and its relation to the catalytic selectivity have not been fully understood. For example, for the case of silica/Ru(0001) interfaces, R. Włodarczyk et al. showed that changes in the coverage of chemisorbed oxygen on Ru(0001) result in gradual changes of the silica/Ru electronic states [16]. However, the detailed underlying mechanism remains unclear.

The study presented here extends the previous work by the groups of Freund and Sauer [16], by carrying out X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) calculations to reveal the mechanisms of the electronic state tuning at the silica/Ru(0001) interfaces. The main focus is on energy levels of the silica films upon the addition or reduction of chemisorbed oxygen on the Ru(0001) substrate. We found that the charge transfer from Ru to chemisorbed oxygen atoms induces surface dipole moments, which has an opposite sign of the interface dipole moments caused by the charge transfer between silica films and the Ru substrate. These two competing effects, depending on the amount of chemisorbed oxygen, dominate the energy level alignment at the silica/Ru(0001) interfaces and the core-level binding energies in the silica films.

2 Experimental and Computational Methods

The Ru(0001) single crystal surface was cleaned with cycles of Ar^+ sputtering and annealing at 1400 K. It was then exposed to 3×10^{-6} mbar O_2 at 1200 K in order to form a chemisorbed oxygen overlayer. The silica and aluminosilicate films were grown on the oxygen pre-covered Ru surface as described in detail elsewhere [9, 10]. Briefly, Si (or Si and Al) was thermally evaporated onto the O/Ru(0001) surface at room temperature under 2×10^{-7} mbar of O_2 , followed by oxidation at 1200 K in 3×10^{-6} mbar O_2 for 10 min and then slowly cooled down in the O_2

environment. In-situ XPS measurements were carried out in an ultrahigh vacuum (UHV) system using Mg $K\alpha$ ($h\nu = 1253.6$ eV) as the excitation source. Vacuum level shifts were determined from the secondary electron cutoff at the low kinetic energy part of the XPS spectra with a -15 V sample bias. AP-XPS measurements were carried out at the CSX-2 beamline of the National Synchrotron Light Source II (NSLS-II) [12]. A photon energy of 750 eV was used in our studies, which was calibrated and referenced to the Fermi level of the Ru(0001) substrates. Infrared reflection absorption spectroscopy (IRRAS) experiments were carried out in a home-built UHV system equipped with a Bruker Vertex 70 spectrometer [17]. This system is also capable of polarization modulation (PM) IRRAS experiments at pressures up to 1 Atm. The beam is reflected from the surface plane at an angle 8° and the signal measured with a liquid-nitrogen-cooled MCT detector. The chamber has BaF_2 windows allowing IR light to enter and exit the chamber and to withstand the potentially high pressures the instrument is capable of.

DFT calculations were performed using projector augmented-wave method implemented in the Vienna Ab initio simulation package (VASP) [18, 19]. The consistent exchange van der Waals density functional (vdW-DF-cx) [20, 21] was used to describe the non-local vdW interactions in the silica/Ru(0001) heterojunction. The choice of vdW-DF-cx was justified by its good performance for both metallic systems [20] and bulk chabazite tested against PBE [22, 23], several other flavors of vdW-DFs implemented in VASP [24] including optB88-vdW and optB86b-vdW [25], and empirical vdW methods PBE-D [22] [6] and PBE-D3(BJ) [27, 28] (see Supporting Information for details). A kinetic energy cutoff of 800 eV was used for bulk ruthenium together with a $28 \times 28 \times 18$ k-point grid for Brillouin zone sampling. For siliceous chabazite, a 700 eV cutoff was used with Γ point sampling. Such high kinetic energy cutoffs are required to reach the numerical convergence for vdW-DF-cx using hard pseudopotentials [24].

The substrate of the silica/Ru(0001) heterojunction was modeled by five layers of ruthenium in a 2×2 supercell ($a = 5.392$ Å and $b = 9.339$ Å). In the surface normal direction, the super cell size was chosen as $c = 27$ Å to ensure the vacuum region to be at least 10 Å thick. A kinetic energy cutoff of 800 eV and an $8 \times 4 \times 1$ k-point grid were used. The silica film and the top two layers of the substrate were relaxed during the structure optimization until forces were smaller than 0.01 eV/Å. Due to the existence of the sizable surface and interface dipole moments, the dipole correction method [29] was used to correct the spurious electrostatic interaction with image cells. The core-level binding energies (E_{BE}) were calculated using the transition state model [30, 31]:

$$E_{BE} = \int_0^1 \varepsilon(\eta) d\eta \approx \varepsilon(0.5),$$

where η ($0 \leq \eta \leq 1$) is the occupation number. $\varepsilon(\eta)$ is the Kohn–Sham (KS) core level eigenvalue (referred to the Fermi level at ground state) when the core level is occupied with η electrons. The excited core electrons in a finite supercell can cause spurious changes in the charge distribution at the interface, which will introduce an error to the calculated E_{BE} . In order to eliminate this error, we calculated core level orbital energies using 2×2 ($a = 5.392 \text{ \AA}$ and $b = 9.339 \text{ \AA}$), 4×2 ($a = 10.784 \text{ \AA}$ and $b = 9.339 \text{ \AA}$) and 8×4 ($a = 21.568 \text{ \AA}$ and $b = 18.678 \text{ \AA}$) supercells, and the results are extrapolated to the infinite supercell size limit. All E_{BE} values are given relative to that of chemisorbed oxygen atoms of the heterojunction with the highest oxygen coverage.

3 Results and Discussion

The structures of chemisorbed oxygen on Ru(0001) have been well studied, with four different phases reported in the literature, namely, $p(2 \times 2)$ -O [32], $p(2 \times 1)$ -O [33], (2×2) -3O [34] and (1×1) -O [35]. As previously reported, bilayer silica films can be grown on either $p(2 \times 1)$ -O/Ru(0001) or (2×2) -3O/Ru(0001) surfaces depending on the preparation conditions [9, 36]. For the current study, a (2×2) -3O/Ru(0001) superstructure was obtained prior to the silica film preparation. It was previously suggested that the chemisorbed oxygen prevents Si atoms from diffusing into the Ru(0001) during the thermal evaporation [9]. The as-deposited SiO_x film was post-annealed at 1200 K in 3×10^{-6} mbar O_2 . Well-ordered bilayer silica films are then formed and all the silicon species are oxidized to Si^{4+} , with a binding energy of 102.75 eV as is revealed by XPS (green spectra in Fig. 1b) [36]. The bilayer nature of the film was corroborated by infrared reflection absorption spectroscopy (IRRAS). The corresponding O 1s spectra (green spectra in Fig. 1a) show a main peak at 532.00 eV and a shoulder peak at 529.80 eV, which are assigned to the Si–O–Si linkages in bilayer silica films and the chemisorbed oxygen on Ru (O–Ru) respectively [37]. A shoulder peak of Ru $3d_{5/2}$ further confirms the existence of the chemisorbed oxygen at the interface as shown in Fig. 1c.

The interfacial chemisorbed oxygen coverage was estimated to be 0.42 monolayer (ML) for O/Ru(0001) with as-prepared bilayer silica film with reference to the 0.75 ML of (2×2) -3O/Ru(0001) and taking into account the attenuation by the silica film in the calculation. The as-prepared bilayer silica was then annealed in UHV from 950 to 1200 K. When the temperature is increased, the O 1s

peak from the Si–O–Si moieties gradually shifts to higher binding energy by ~ 0.70 eV (Fig. 1a), while the position of the O 1s peak from (O–Ru) remains almost unchanged. This is similar to previous work where the O 1s peak from silica films shifts to higher binding energy by ~ 0.8 eV upon UHV annealing to 1150 K [16]. In parallel, the Si 2p peak also shows a similar 0.70 eV shift upon annealing (Fig. 1b). Christin Büchner et al. also found that the work function decreases by 0.8 eV while O 1s peak and Si 2p peak shift to higher binding energy by 0.77 eV after creating the O-poor film [2]. Both the intensity and the full width at the half maximum (FWHM) of the O 1s and Si 2p remain unchanged, indicating that the chemical composition and bonding configuration of the silica film stay intact. The increase in binding energies can be attributed to changes of the chemical states on the Ru substrate [13, 37, 38]. As shown in Fig. 1a and 1c, the features of the O 1s and Ru 3d peaks arising from the O–Ru moiety decrease by a factor of 2.6 as compared to the as-prepared bilayer silica upon annealing to 1200 K in UHV, indicating that the coverage of interfacial oxygen decreases from 0.42 to 0.16 ML. Simultaneously, the work function (or the vacuum level) of the system decreases from 6.45 to 5.50 eV. The silica/Ru(0001) was then further reduced by annealing in 3×10^{-6} mbar of H_2 at 400 K, resulting in 0.06 ML chemisorbed oxygen on Ru(0001) as the orange spectra shows in Fig. 1. Consequently, the binding energies of O 1s (Si–O–Si) and Si 2p shift another 0.05–532.75 and 103.50 eV respectively, while the work function further decreases to 5.35 eV.

The amount of interfacial chemisorbed oxygen can be reversibly tuned. As shown in Fig. 2, all silica-related core levels shift back to lower binding energies upon exposure to 2×10^{-4} mbar of O_2 at 820 K. The coverage of chemisorbed oxygen increases to 0.75 ML, which is attributed to the higher O_2 pressure [12]. Similarly, upon reduction by exposing the surface to 0.1 mbar of H_2 at 380 K, all silica-related core levels shift to higher binding energies again. The significantly attenuated O 1s (O–Ru) and Ru 3d (O–Ru) peaks indicate that most of the chemisorbed oxygen at the interface desorbs. The valence band spectra in Fig. 2d also shows a decrease in intensity at ~ 5 eV, corresponding to the reduced O–Ru states [39]. The peak at 10.6 eV is originated from the hybridization between the O_{2p} and $\text{Si}_{3s/3p}$ states in the Si–O–Si linkage of the bilayer silica films [40]. These hybridized states also shift to higher binding energies, consistent with the silica-related core levels shifts.

By comparing the magnitude in core levels shift (0.75 eV) and work function shift (1.10 eV) in the silica film during the reduction of the Ru substrate (chemisorbed oxygen coverage decreases from 0.42 to 0.06 ML), it is likely that both the surface (i.e., O–Ru) and the interface

Fig. 1 Interfacial chemisorbed oxygen dependent energy levels at the weakly interacted bilayer silica/Ru(0001) interface. The evolution of the XPS ($h\nu = 1253.6$ eV) core level spectra of **a** O 1s, **b** Si 2p, **c** Ru 3d, and **d** the XPS spectra at the low-kinetic energy part (secondary electron cutoff) upon heating the silica/Ru(0001) from 950 to 1200 K in vacuum. **e** Plots the interfacial chemisorbed oxygen coverage dependent binding energies and work functions. The *black spectrum* is clean Ru(0001) and the *red spectrum* is (2×2) -3O/Ru(0001) (i.e., with 0.75 ML O). The *orange spectrum* was collected after annealing the film in 3×10^{-6} mbar of H_2 at 400 K

(i.e., silica/O-Ru) dipoles play important roles in determining the energy level shifts at the silica/Ru(0001) heterojunction. We further explored the underlying mechanisms using DFT for the silica/Ru(0001) heterojunction with different amounts of interfacial chemisorbed oxygen. We denote the chemisorbed oxygen species as O(Ru), and the oxygen species in the corner-sharing SiO_4 tetrahedra in silica films as O(Si). The silica/Ru(0001) heterojunction was modeled as bilayer silica films (SiO_2) on Ru(0001). Si atoms in the bilayer are located on hollow sites of Ru(0001), and this model has been used in the literature [10]. In order to investigate the influence of O(Ru) on the electronic structure of silica films, we studied three oxygen coverages on Ru(0001) according to experimental conditions: Ru(0001), $p(2 \times 2)$ -O/Ru(0001) and $p(2 \times 1)$ -O/Ru(0001) as shown in Fig. 3. These models correspond to $(SiO_2)_8/0O/Ru(0001)$, $(SiO_2)_8/2O/Ru(0001)$ and $(SiO_2)_8/4O/Ru(0001)$, respectively, where nO ($n = 0, 2$ or 4) represents the number of O(Ru) in the unit cell (i.e., 0, 0.25,

0.50 ML). At $n = 0$, the silica film is physisorbed on the Ru substrate with a interlayer distance ($d(Ru-O_{Si})$) of 2.84 Å. As n increases, the silica film is pushed away from the substrate. At $n = 4$, $d(Ru-O_{Si})$ increases by as much as 1.00 Å. Previous DFT calculations using PBE-D2 [26] also showed that as the coverage of the chemisorbed oxygen on Ru(0001) increases from $n = 0$ to $n = 4$, $d(Ru-O_{Si})$ by 0.93 Å [16]. During this process, the thickness of the silica films ($d(O-O)$) remains intact as shown in Fig. 3.

At the silica/O-Ru(0001) heterojunction, multiple mechanisms may contribute to the formation of surface or interface dipole moments. The first one is the “push-back” effect [41], where the Pauli repulsion due to the silica film suppresses the tail of metal surface electrons that spill out into the vacuum. In addition, the chemisorbed O atoms on Ru(0001) can also cause charge redistributions through the Ru-O hybridization [42], which we refer to as the surface charge transfer. The surface charge transfer can cause a surface dipole at the O-Ru(0001) surface. Furthermore, the

Fig. 2 Reversible tuning of the interfacial chemisorbed oxygen coverage. AP-XPS ($h\nu = 750$ eV) core level spectra of **a** O 1s, **b** Ru 3d, **c** Si 2p and **d** valence band. The *black spectrum* is obtained in UHV after annealing the film in 2×10^{-4} mbar of O_2 at 820 K (with

interfacial chemisorbed oxygen coverage of 0.75 ML), and the *green spectrum* is taken under 0.1 mbar of H_2 at 380 K. (with interfacial chemisorbed oxygen coverage of 0.08 ML)

Fig. 3 Side (*left*) and top (*right*) view of relaxed structures of **a** $(SiO_2)_8/0O/Ru(0001)$, **b** $(SiO_2)_8/2O/Ru(0001)$, and **c** $(SiO_2)_8/4O/Ru(0001)$. Black rectangles indicate the unit cell. Color code: Ru (silver), Si (yellow), O in silica films (red), and O chemisorbed on Ru(0001) (purple). Black arrows in top view of (**c**) indicate the location of chemisorbed oxygen atoms underneath silicon atoms (two per unit cell). Distances on the left correspond to the thickness of the silica films ($d(O-O)$) and interlayer distances ($d(Ru-O_{Si})$)

quadrupole moment of the silica film can induce dipole moments on the substrate. Finally, unsaturated electrons in O atoms at the bottom layer of the silica film may tunnel

into the unoccupied Ru d -bands, which we refer to as the interfacial charge transfer. Only in the interfacial charge transfer mechanism, there is a substantial net charge transfer between the silica film and O-Ru(0001), i.e., across the heterojunction, which leads to an interface dipole at the heterojunction.

Interface dipoles caused by charge transfer across distances of 3–4 Å have been reported at the graphene/molecule interface [43] and the NO/SnS₂ interface [44], and predicted by DFT at the metal/graphene interface [45] and the 3, 4, 9, 10-perylene tetracarboxylic dianhydride/Ag(111) interface [46]. Hofmann et al. attributed the reduction of metal work function in Tetrathiafulvalene/Au(111) and Viologen/Au(111) to the charge transfer from organic molecules to Au(111) that is about 3 Å away [47].

Here, the interactions among Ru substrate, O(Ru), and the silica film can cause a significant charge redistribution, which leads to the formation of dipole moments and changes in the work function. The dominating contributions arise from two types of dipole moments at $(SiO_2)_8/nO/Ru(0001)$ heterojunctions: surface dipole moments (p_{sur}) due to the charge transfer between Ru(0001) and O(Ru), and interface dipole moments (p_{inter}) due to the interfacial charge transfer between silica films and $nO/Ru(0001)$ substrates. We calculated the plane-averaged charge density differences between the charge densities of the combined systems and the superimposed charge densities of the individual systems: $\Delta\rho_{sur} = \rho_{nO/Ru} - (\rho_O + \rho_{Ru})$, and $\Delta\rho_{inter} = \rho_{SiO_2/nO/Ru} - (\rho_{SiO_2} + \rho_{nO/Ru})$. As shown in Fig. 4, $\Delta\rho_{inter}$ spreads across the interface with a nodal plane between silica films and the $nO/Ru(0001)$

Fig. 4 Plane-averaged electron density difference $\Delta\rho_{\text{sur}}$ and $\Delta\rho_{\text{inter}}$ (per unit cell). Δq is the number of electrons calculated by integrating $\Delta\rho$ from the bottom of the substrate at $z = 0$ to the nodal plane at $z = z_0$ (open black circle). p [p_{inter} is calculated using $p_{\text{inter}} = p_{\text{SiO}_2/n\text{O}/\text{Ru}} - p_{\text{sur}} - p_{\text{SiO}_2}$. For the system with $n = 0$, $p_{\text{SiO}_2} = -0.04 \text{ e}\text{\AA}$ while for systems with $n = 2$ and 4 , p_{SiO_2} becomes negligible] (in $\text{e}\text{\AA}$) is the dipole moment caused by $\Delta\rho$

substrates. It corresponds to a positive dipole moment along z (Fig. 4a–c), which can be attributed to electron tunneling from silica films to the $n\text{O}/\text{Ru}(0001)$ substrate. On the other hand, $\text{O}(\text{Ru})$ draws electrons from $\text{Ru}(0001)$, forming negative dipole moments along z (Fig. 4d and 4e). The magnitude of the charge transfer per unit cell (Δq) was calculated by integrating the $\Delta\rho_{\text{sur}}$ and $\Delta\rho_{\text{inter}}$ along z .

In order to understand the nature of the interfacial charge transfer, we performed electronic structure analysis of the $(\text{SiO}_2)_8/\text{Ru}(0001)$ interface. As shown in the iso-surface of the charge difference in Fig. 5a, the bottom layer O atoms of the silica film lose electrons, while the top layer of $\text{Ru}(0001)$ gain electrons. A nodal plane is formed at $1.98 \text{ \AA}$ above the top layer of $\text{Ru}(0001)$ and $0.86 \text{ \AA}$ below the bottom layer of the silica film, supporting the interfacial charge transfer mechanism. The shaded green area around the top layer of $\text{Ru}(0001)$ is likely caused by the ‘push-back’ effect and the quadrupole induced dipole moment [48]. Furthermore, Fig. 5a suggests the electron depletion in the $\text{O } p_z$ orbitals and the electron accumulation in the $\text{Ru } d_{xz}$ and d_{yz} orbitals.

In Fig. 5, we plot the projected density of states (PDOS) of the p_x , p_y and p_z orbitals of the bottom O layer of the freestanding (Fig. 5c) and adsorbed silica film (Fig. 5d), and the PDOS of the d_{xz} (Fig. 5e) and d_{yz} (Fig. 5f) orbitals of the top layer of $\text{Ru}(0001)$. In Figs. 5c and 5d, the PDOS are aligned at the valence band maximum (VBM) of the freestanding and adsorbed silica film, and the PDOS in Figs. 5e and 5f are aligned at the Fermi level. The PDOS of the freestanding silica film displays a sharp peak in p_z near VBM. This peak disappears in the PDOS of the adsorbed silica film, indicating significant electron depletion from p_z orbitals. Accordingly, there is an increase in the occupied PDOS of the $\text{Ru } d_{xz}$ and d_{yz} orbitals near the Fermi level

upon the physisorption, indicating electron density accumulation in d_{xz} and d_{yz} orbitals of the top layer of $\text{Ru}(0001)$.

The interfacial charge transfer can occur at a short distance when electrons can tunnel from the silica film to the substrate. As the separation increases, one expects an exponential decay of the amount of tunneling electrons [49]. To verify this point, we gradually increased the distance between silica films and $\text{Ru}(0001)$ ($d(\text{Ru}-\text{O}_{\text{Si}})$) from the equilibrium distance of $2.84 \text{ \AA}$ to a larger separation of $3.84 \text{ \AA}$. The corresponding charge density difference ($\Delta\rho_{\text{inter}}$) and the integrated amount of the charge transfer (Δq) at different separation distances are shown in Figure S1. In Fig. 5b, we found an evident exponential decay of the net charge transfer with a decay length of $1.00 \text{ \AA}$.

At $n = 0$, the dominating factor is the interfacial charge transfer with $\Delta q_{\text{inter}} = 0.21$ electrons and $p_{\text{inter}} = 0.40 \text{ e}\text{\AA}$ (Fig. 4a). The interface dipole moment causes the work function to decrease by 1.24 eV as compared to $\text{Ru}(0001)$ (see Table 1). At $n = 2$, as the oxygen coverage increases, $d(\text{Ru}-\text{O}_{\text{Si}})$ increases by $0.81 \text{ \AA}$. Consequently, Δq_{inter} decreases to 0.03 electrons, and p_{inter} drops to $0.06 \text{ e}\text{\AA}$. On the other hand, $\text{O}(\text{Ru})$ draw 0.22 electrons from $\text{Ru}(0001)$, which leads to $p_{\text{sur}} = -0.03 \text{ e}\text{\AA}$ (Fig. 4b). As p_{inter} and p_{sur} nearly cancel each other, the net dipole moment (p_{tot}) of $(\text{SiO}_2)_8/2\text{O}/\text{Ru}(0001)$ becomes $0.03 \text{ e}\text{\AA}$, and work function slightly increases by 0.04 eV as compared to $\text{Ru}(0001)$. At $n = 4$, $d(\text{Ru}-\text{O})$ increases to $3.84 \text{ \AA}$ and Δq_{inter} becomes negligible. In the end, p_{tot} is dominated by the surface dipole moment ($-0.18 \text{ e}\text{\AA}$), leading to a work function increase by 0.81 eV as compared to $\text{Ru}(0001)$.

According to previous experimental studies, surface bound oxygen species greatly affect the work function of the Ru substrate, which ranges from ~ 5.3 to $\sim 6.7 \text{ eV}$

Fig. 5 **a** Isosurface plot of the charge density difference upon adsorption of SiO_2 on $\text{Ru}(0001)$ with an isodensity value of $0.01 \text{ e}/\text{\AA}^3$. Red: electron accumulation regions; Blue: electron depletion regions. Plane-averaged electron density difference $\Delta\rho_{\text{inter}}$ is shown on the right. The black line corresponds to $\Delta\rho_{\text{inter}}$, and the red line is the integration of $\Delta\rho_{\text{inter}}$ with respect to z . **b** Net tunneling electrons with respect to the interface separation $d(\text{Ru}-\text{O}_{\text{Si}})$. **c** PDOS of the p_x , p_y and p_z orbitals for the bottom layer of O atoms (O_b) of the freestanding silica films. Shaded area is the DOS of the freestanding silica films. The energy is relative to the valence band maximum (VBM) of the silica film. **d** PDOS of the p_x , p_y and p_z orbitals of the bottom layer O atoms (O_b) in the adsorbed silica films in $(\text{SiO}_2)_8/\text{Ru}(0001)$. Shaded area is the PDOS of the adsorbed silica films. The energy is relative VBM of the adsorbed silica film. **e** PDOS of the d_{xz} orbitals of the top layer Ru atoms in the clean $\text{Ru}(0001)$ (black line) and $(\text{SiO}_2)_8/\text{Ru}(0001)$ (red line). **f** PDOS of the d_{yz} orbitals of the top layer Ru atoms of the clean $\text{Ru}(0001)$ (black line) and $(\text{SiO}_2)_8/\text{Ru}(0001)$ (red line)

[42], and the work function change of the substrate can further affect the interfacial charge transfer between the adsorbed molecule and the substrate [50]. To rationalize

the charge transfer contribution to the potential change upon silica films adsorption, we use a plane capacitor model [45] combined with the Helmholtz equation [51], $\Delta V = p/\epsilon\epsilon_0$, where ΔV , p , ϵ_0 and ϵ are the change of the surface potential, the dipole moment per unit cell caused by the interfacial charge transfer, the dielectric constant of vacuum and the relative dielectric constant, respectively. ϵ is calculated to be 1.35 in $(\text{SiO}_2)_8/2\text{O}/\text{Ru}(0001)$ and used to interpret experimental results. Δq can be calculated from $\Delta q = p/z_d$ where z_d is the effective distance between the sheets of the plane capacitor. z_d for $(\text{SiO}_2)_8/2\text{O}/\text{Ru}(0001)$ is 2 Å, which is smaller than $d(\text{Ru}-\text{O}_{\text{Si}})$ by a constant d_0 defined as $d_0 = d(\text{Ru}-\text{O}_{\text{Si}}) - z_d$. $d(\text{Ru}-\text{O}_{\text{Si}})$ is linearly extrapolated from that of $(\text{SiO}_2)_8/2\text{O}/\text{Ru}(0001)$ (0.25 ML) and $(\text{SiO}_2)_8/4\text{O}/\text{Ru}(0001)$ (0.5 ML) in Fig. 1 for 0.2 and 0.42 ML. When the coverage of interfacial oxygen is ~ 0.2 ML in the experiment, the work function of the surface decreases 0.09 eV upon silica film adsorption while the estimated interfacial charge transfer is 0.017 electrons per unit cell from the silica film to the Ru substrate. In comparison, when the coverage of the interfacial oxygen is increased to ~ 0.42 ML, the work function of the surface increases 0.31 eV upon adsorption of the silica film. We estimate the magnitude of the charge transfer to be 0.055 electrons per unit cell from the Ru substrate to the adsorbed silica film.

In the range of oxygen coverage we studied, p_{tot} of $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$ decays as a function of n , as p_{sur} increases and p_{inter} decreases. The impact of p_{tot} on the energy levels can be understood from the plane-averaged electrostatic potential calculated for the clean $\text{Ru}(0001)$, freestanding silica films, and physisorbed silica films at different n shown in Fig. 6. The Fermi levels (E_F) of $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$ are aligned with that of the $\text{Ru}(0001)$. The work function (Φ) of the clean $\text{Ru}(0001)$ is 5.12 eV, which is measured as the difference between E_F and the vacuum energy level (E_{vac}). The ionization potential (IP) of the silica film is 7.96 eV, which is measured as the energy difference between VBM and E_{vac} . When E_{vac} of the clean $\text{Ru}(0001)$ and freestanding silica films are aligned, the energy separation (ΔE) between E_F of the $\text{Ru}(0001)$ and VBM of silica films is 2.84 eV. When the silica film is

Table 1 Dipole moment (in eÅ) and work function (in eV) of $\text{Ru}(0001)$, $n\text{O}/\text{Ru}(0001)$ and $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$ for $n = 0, 2, 4$

	$\text{Ru}(0001)$	$(\text{SiO}_2)_8/0\text{O}/\text{Ru}(0001)$		$(\text{SiO}_2)_8/2\text{O}/\text{Ru}(0001)$		$(\text{SiO}_2)_8/4\text{O}/\text{Ru}(0001)$	
	Ru	Ru	$\text{Ru}/(\text{SiO}_2)$	Ru/O	$\text{Ru}/\text{O}/(\text{SiO}_2)$	Ru/O	$\text{Ru}/\text{O}/(\text{SiO}_2)$
p	0.02	0.02	0.38	-0.03	0.03	-0.18	-0.18
Φ	5.12 [†]	5.12	3.88	5.32	5.16	5.89	5.93
	(5.37)						

The number in parenthesis is the experimental value

[†] The work function of the clean $\text{Ru}(0001)$ with top two layers allowed to relax. $\Phi = 5.03$ eV was reported by Kim et al. [42]

Fig. 6 Plane-averaged electrostatic potential for Ru(0001), free-standing silica films, and physisorbed silica films in $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$, where $n = 0, 2, 4$. Red lines indicate Fermi levels, and blue lines indicate VBMs

physisorbed on the clean Ru(0001), p_{inter} causes a drop of E_{vac} and VBM of the physisorbed silica film. ΔE thus becomes 3.87 eV. As n increases, VBM of silica films moves closer to the Fermi level, due to the decrease of p_{tot} . The decay trend of ΔE as a function of n (Table 2) is generally consistent with experimentally observed O 1s and Si 2p binding energy (E_{BE}) downward shift during the Ru(0001) surface oxidation. This indicates that the core-level binding energy shift (ΔE_{BE}) in silica film during surface oxidation is caused by the surface and interface dipole fields.

The calculated layer-resolved E_{BE} of the O 1s core levels, relative to that of O(Ru) in $(\text{SiO}_2)_8/4\text{O}/\text{Ru}(0001)$, are shown in Table 2. The comparison with experimental results is shown in Fig. 7. All E_{BE} values are extrapolated to infinite supercell limit. The values of E_{BE} calculated for the 2×2 , 4×2 and 8×4 unit cells are summarized in Table 2 in the Supporting Information. As n increases from 2 to 4, the E_{BE} of O(Ru) changes only 0.09 eV, in good agreement with the experiment. The average E_{BE} of O(Si) is 3.32, 2.11 and 1.52 eV for $n = 0, 2$ and 4, respectively,

Table 2 Simulated core level binding energy (E_{BE} in DFT) for chemisorbed oxygen on Ru(0001) (O(Ru)) and oxygen in silica films (O(Si)) in $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$ where $n = 0, 2, 4$ and XPS core level binding energy (E_{BE} in XPS) for O(Ru) and O(Si) in $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$ where $n = 0.56, 2.00, 3.36$. $O_t(\text{Si})$, $O_m(\text{Si})$, and $O_b(\text{Si})$ in DFT stand for E_{BE} for top, middle and bottom O layer in silica films,

				$N = 0$	$N = 2$	$N = 4$
DFT	E_{BE}	O(Si)	$O_t(\text{Si})$	3.74	2.47	1.82
			$O_m(\text{Si})$	3.28	1.98	1.37
			$O_b(\text{Si})$	2.92	1.84	1.31
			$O_{\text{ave}}(\text{Si})$	3.32	2.11	1.52
		O(Ru)		—	0.09	0
			ΔE	3.87	2.87	2.07
XPS	E_{BE}	O(Si)	2.95 ($n \approx 0.56$) 2.55 ($n \approx 2.00$) 2.20 ($n \approx 3.36$)

Fig. 7 Average core level binding energy (E_{BE}) for oxygen in silica films in $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$ from DFT (Black dot) and XPS experiments (Red triangle). Red lines represent error bars from experiments

corresponding to $\Delta E_{\text{BE}} = -1.80$ eV. In the core-level XPS spectra in Fig. 1e, the corresponding ΔE_{BE} is -0.75 eV, when the coverage of O(Ru) increases from 0.07 ML ($n \approx 0.56$) to 0.42 ML ($n \approx 3.36$) during the oxidation process. The decreasing trend of E_{BE} qualitatively agrees with experiment. However, the magnitude of the calculated ΔE_{BE} is larger than the experimental value. Various factors may contribute to this difference. Experimentally, the estimate of oxygen coverage from normalized XPS peak intensities has an error of ± 0.1 ML, and the error bar for the core level binding energy is ± 0.05 eV. On the other hand, approximations used in the E_{BE} simulation (e.g., treating XPS with a neutral excitation instead of a charged excitation) may also introduce errors. The E_{BE} of O(Si), resolved by layers, show a spread of 0.82, 0.63 and 0.51 eV for $n = 0, 2$ and 4 because of the different chemical environments of the O atoms in the two different layers. In the core-level XPS spectra (Fig. 1a), the FWHM of O(Si) is 1.6 eV while O(Ru) is 1.0 eV. The FWHM difference of 0.6 eV between O(Ru) and O(Si) can be related to the different binding energies calculated for O in the different layers of the silica framework.

and $O_{\text{ave}}(\text{Si})$ stands for the average E_{BE} of all O atoms in silica films. All E_{BE} values are relative to that of O(Ru) in $(\text{SiO}_2)_8/4\text{O}/\text{Ru}(0001)$. The energy separations (ΔE , see Fig. 5) are calculated as the difference between E_{F} of $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$ and VBM of silica films. The energy unit is eV

Fig. 8 Schematic diagrams showing interfacial chemisorbed oxygen dependent energy levels at the silica/Ru(0001) heterojunction

The surface and interfacial charge transfer and corresponding energy level shifts are schematically shown in Fig. 8. The charge transfer from Ru(0001) to O(Ru) results in negative surface dipole moments, while the interfacial charge transfer from silica films to the Ru substrate leads to positive interface dipole moments. During the oxidation of the Ru substrate, these two competing effects gradually increase the work function of $(\text{SiO}_2)_8/n\text{O}/\text{Ru}(0001)$ and move the energy levels in the silicate films closer to the Fermi level. As discussed above, the experimentally determined interface dipole moment changes sign starting at a chemisorbed-oxygen coverage of ~ 0.25 ML. Due to the small magnitude of the interfacial charge transfer at a large interfacial distance, the magnitude of the interface dipole moment is smaller than the surface dipole moment.

To further confirm that the energy levels at the silica/Ru(0001) heterojunction can be realigned by tuning the chemical states of the Ru(0001) substrate, we investigated an interface consisting of an aluminosilicate bilayer on Ru(0001). This is of special importance for catalysis, since these aluminosilicate films have proven to represent good surface science model for zeolites [52]. The aluminosilicate film was composed of an ordered bilayer network of $[\text{SiO}_4]$ and $[\text{AlO}_4]^-$ tetrahedra ($\text{Al}_x\text{Si}_{1-x}\text{O}_2$), which is also weakly bound to the Ru substrate [10]. For the case of the aluminosilicate, we expect an additional charge transfer from the Ru substrate to the aluminosilicate film, to compensate for the charge imbalance introduced in the framework when introducing Al in tetrahedral positions. In this paper, the aluminosilicate film was prepared with a

Fig. 9 Dependence of energy levels at the bilayer aluminosilicate/Ru(0001) heterostructure ($\text{Al}_{0.16}\text{Si}_{0.84}\text{O}_2$) on the coverage of chemisorbed oxygen. The evolution of the AP-XPS ($h\nu = 750$ eV) core level spectra **a** O 1s, **b** Al 2s, **c** Si 2p and **d** Ru 3d are shown in the figure upon heating the aluminosilicate/Ru(0001) from 300 to 840 K in 2×10^{-4} mbar of O_2 (the coverage of interfacial chemisorbed oxygen increases from 0.05 to 0.5 ML)

stoichiometry of $\text{Al}_{0.16}\text{Si}_{0.84}\text{O}_2$. The “as-prepared” aluminosilicate film was first reduced in hydrogen to remove most of the chemisorbed oxygen at the interface. As shown in Fig. 9a, the O 1s in the $\text{Al}_{0.16}\text{Si}_{0.84}\text{O}_2/\text{Ru}(0001)$ heterostructure develops into two peaks with a main component at 532.05 eV and a shoulder at 531.05 eV, which are assigned to the Si–O–Si linkage and Al–O–Si linkage respectively [10]. By oxidizing the film in 2×10^{-4} mbar O_2 , a third oxygen peak appears at a binding energy of 529.85 eV, corresponding to the chemisorbed oxygen on the Ru(0001) substrate. Similarly, all the core levels in the aluminosilicate framework shift to the lower binding energy by ~ 0.6 eV as shown in Fig. 9a–c, while the chemisorbed oxygen peak still remains at the same binding energy. These energy level shifts are also reversible as observed during the reduction reaction process, which is consistent with the silica/Ru(0001) heterojunction.

It should be noted that the O 1s (Si–O–Si) and Si 2p binding energies in the aluminosilicate/Ru(0001) are ~ 0.7 eV higher than for the silica/Ru(0001), for the Ru(0001) substrate with a coverage of chemisorbed O of ~ 0.05 – 0.07 ML (after reduction in H_2). This can be induced by partial electron transfer from the substrate to the aluminosilicate film in order to compensate the charge imbalance caused by the Al substitution at the bottom of the aluminosilicate bilayer [10], which will decrease the total dipole moment (p_{tot}) across the aluminosilicate/Ru(0001) heterojunction. As a result, the observed total energy level shifts in then aluminosilicate (~ 0.6 eV) is smaller than that in silica (~ 0.8 eV) when the Ru content of chemisorbed oxygen changes from 0.05 to 0.5 ML.

4 Conclusions

In summary, a combined in situ XPS and DFT study for the silica/Ru(0001) system reveals the mechanism for core level shifts in silica films as the coverage of chemisorbed oxygen is varied. Although the structures of the silica films are found to stay intact under these reactions, the interface electronic structures can be significantly affected by the chemical states of the Ru substrate. The interfacial properties, in particular dipole moments due to charge transfer, play essential roles in determining the energy level alignments across the silica/Ru interfaces. Our detailed investigations using the model bilayer-silica/Ru(0001) system provide physical insights into the effects of interface electronic properties in silica model systems. Furthermore, this is extended to the case of the bilayer-aluminosilicate/Ru(0001), of great importance to catalysis, given its potential as a surface science model system for zeolites.

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