Synthesis and Structure of Ultrathin Aluminosilicate Films

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Inorganic-chemistry textbooks define aluminosilicates as silicates in which some of the Si$^{4+}$ ions are replaced by Al$^{3+}$ ions. The excess negative charge arising from the replacement is balanced by positive ions, such as H$^+$ or alkali-metal cations. Zeolites are important microporous members of the aluminosilicate family, which have a large variety of applications ranging from catalysis and adsorption to agriculture and construction.[3] Both experimental and theoretical studies of zeolites, in particular, the precise determination of the catalytically active sites, are often hampered by the structural and chemical complexity of these compounds.[2] The employment of surface-sensitive techniques to elucidate the mechanism of catalytic reactions on zeolites at a fundamental level is challenging. Owing to the insulating properties of aluminum–silicon oxides, this approach can only be successful when indicated that the silicon and aluminum atoms are in fully oxidized states.

To facilitate the intermixing of aluminum and silicon in the film, we codeposited aluminum and silicon onto an O/Mo(112) surface in an oxygen environment (see Experimental Section). After annealing in vacuum, the temperature was increased in steps, until LEED analysis of the film indicated an ordered structure. After annealing films with low Al/Si ratios (less than 0.2) at 1100 K, a sharp LEED pattern corresponding to a c(2×2) structure on the Mo(112) surface, similar to that of the pure silica film, was observed. XPS investigation of these films indicated that the silicon and aluminum atoms are in fully oxidized states.

STM images of the mixed-oxide films reveal atomically flat terraces with only a few nanoparticles at their edges (Figure 1a). High-resolution images show the same honeycomb structure and antiphase domain boundaries reported in the preparation of thin zeolite films as model systems for atomistic studies of zeolite surfaces.

We have recently shown that an ordered thin silica film consisting of a two-dimensional (2D) network of corner-sharing [SiO$_4$] tetrahedra can be grown on a Mo(112) substrate.[10–13] One oxygen atom of each [SiO$_4$] tetrahedron in the film points towards molybdenum atoms in the substrate. Deposition of aluminum onto the film and subsequent annealing in vacuum leads to a partial reduction of the silica, as evidenced by X-ray photoelectron spectroscopy (XPS). This sequential preparation destroys the long-range order in the original silica film, as shown by low-energy electron diffraction (LEED). STM inspection of the product revealed a rough surface with particle-like features, which were interpreted as alumina nanoparticles embedded in the silica film. This observation is consistent with the results of Gründling et al., who obtained disordered Al$_2$O$_3$–SiO$_2$ films by vacuum annealing samples consisting of aluminum deposited onto approximately 3-nm-thick silica films on Mo(100) substrates.[14]

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for the silica films (Figure 1b). However, in contrast to the pure silica films, numerous bright spots were detected on the surface of the aluminosilicate films. These spots are approximately 0.2 Å higher than the neighboring protrusions. The density of the spots correlates well with the aluminum coverage determined by XPS, and their random distribution indicates a random distribution of the aluminum atoms in the film. The protrusions are slightly elongated along one of the principal directions of the silica lattice, which coincides with the [111] direction of the Mo(112) surface (additional experiments demonstrated that this is not a tip artifact).

On the basis of these LEED and STM results, we propose that the structure of the aluminosilicate film consists of a 2D network of corner-sharing \{SiO$_4$\} tetrahedra, in which some Si$^{4+}$ ions are replaced by Al$^{3+}$ ions. The charge defects introduced by the Al$^{3+}$ ions must be compensated. In bulk aluminosilicates, this compensation is achieved by the intercalation of H$^+$ or alkali-metal cations. Alkali metals were not present during the film preparation, and H$^+$ ions were not detected by vibrational or electron spectroscopy. However, the extra charge in thin films can be easily accommodated by the electron reservoir of the metal substrate. In this [AlO$_4$] model, the Al$^{3+}$ ions are each coordinated to four O$_2^-$ ions in the same geometry as the Si$^{4+}$ ions in the pure silica film (Figure 2). Another possibility is that the Al$^{3+}$ ions are coordinated by three O$_2^-$ ions from the top layer of the film, but are not bonded to an O$_2^-$ ion at the substrate interface ([AlO$_3$] model; Figure 2).

These two models were examined with DFT calculations by considering a (4 × 2) surface cell, in which one of the eight silicon atoms was replaced by an aluminum atom, resulting in compositions of AlSi$_3$O$_{10}$ for the [AlO$_4$] model and AlSi$_5$O$_{19}$ for the [AlO$_3$] model. Both models are minima on the potential energy surface.

For the STM image shown in Figure 1b, the tunneling parameters were chosen such that the oxygen atoms in the topmost layer of the film are detected as protrusions. In the images simulated from the DFT-optimized structures of the [AlO$_4$] and [AlO$_3$] models, the aluminum-bonded surface oxygen atoms, which have a higher corrugation amplitude, are brighter than the silicon-bonded oxygen atoms (Figure 1). This effect is more pronounced for the [AlO$_4$] model, because of the enhanced relaxation associated with the absence of aluminum-bonded interface oxygen atoms. Comparison of the experimental and simulated STM images, therefore, favors the [AlO$_4$] model.

Further support for the [AlO$_4$] model comes from high-resolution PES. In PE spectra of the silica films (Figure 3, top spectra), the O 1s region, which is much better resolved than by conventional XPS$^{[11-13]}$ comprises two distinct peaks, which are assigned to oxygen species in the top layer (at 532.5 eV) and in the molybdenum-bonded interface layer (at 531.2 eV)$^{[11]}$. The signal at lower binding energy (BE) is strongly attenuated when the spectrum is measured at a grazing emission angle, confirming that the associated oxygen species are located in the subsurface region. The presence of interface oxygen atoms is also manifested by a well-resolved signal at 228.2 eV in the Mo 3d region (not shown), which is attributed to partially oxidized molybdenum atoms at the substrate surface (a signal at 228.0 eV is also observed, which is assigned to metallic molybdenum).

As a result of the presence of approximately 20 mol % aluminum in the aluminosilicate film, the O 1s signals in the PE spectra broaden (see Figure 3, bottom spectra), because the oxygen atoms (which are bonded to silicon and/or aluminum atoms) occupy a variety of environments. Our DFT calculations revealed that the oxygen atoms in Si-O-Al units have a BE of 531 eV, which overlaps with that of the interface oxygen atoms in Si-O-Mo units. As a result, the intensity of the lower-BE O 1s signal is notably higher in the PE spectrum of the aluminosilicate film than in that of the pure silica film. Because the aluminum-bonded oxygen atoms are in the top layer of the film, this signal is less attenuated in the aluminosilicate spectrum recorded at a grazing emission angle. According to our calculations, the oxygen atoms in the...
Al-O-Mo units of the [AlO₄] model should be manifested by a signal at 530 eV, which is not observed experimentally. Therefore, our PES results also favor the [AlO₃] model.

The IR spectra of the silica and aluminosilicate films, as well as the calculated frequencies for the [AlO₃] model are presented in Figure 4. Note that only vibrations resulting in changes in the dipole moment that are perpendicular to the surface can be detected, owing to the presence of the metal substrate. The main peak at 1059 cm⁻¹ in the spectrum of the silica film appears as a significantly broadened peak at 1032 cm⁻¹ in the spectrum of the aluminosilicate film. This signal originates from asymmetric Si-O-Mo stretching vibrations[11,12] and is, therefore, strongly influenced by the partial replacement of silicon by aluminum. The line broadening in the aluminosilicate spectrum is consistent with the less-ordered structure of the film relative to that of the pure silica film. The weak IR features at 771 and 675 cm⁻¹ in the silica spectrum, which are assigned to symmetric stretching and bending modes, are also altered in the aluminosilicate spectrum.

The agreement between the calculated and experimental frequencies is not as good as for the silica films. This discrepancy can be partially explained by the relatively small (4×2) unit cell used in the calculations, which results in an ordered superstructure, whereas in the real film the aluminum atoms are randomly dispersed. Nonetheless, the calculations correctly predict the direction of the energy shift of the main signal, as well as the splitting of the signal near 770 cm⁻¹.

In summary, the preparation of an ordered aluminosilicate film on a metal substrate has been achieved through the codeposition of aluminum and silicon onto a Mo(112) surface in an O₂ atmosphere and subsequent vacuum annealing. Experimental and theoretical results show that, in aluminosilicate films with low Al/Si ratios, aluminum atoms partially replace the silicon atoms of the silica structure to form a 2D network of corner-sharing [AlO₃] and [SiO₄] units.
pressure. A full DFT analysis will be presented in future publications.


