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Preparation of an ordered ultra-thin aluminosilicate framework composed of hexagonal prisms forming a percolated network

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Dedicated to Dr. Michael Stöcker on the occasion of his retirement as Editor-in-Chief of Microporous and Mesoporous Materials.

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A B S T R A C T

A flat ultra-thin (0.5 nm thick) aluminosilicate framework was grown using Ru(0001) as a template. The structure and composition were determined by a combination of scanning tunneling microscopy, low energy electron diffraction, infrared reflection absorption spectroscopy and X-ray photoelectron spectroscopy experiments. This film is composed mainly of an ordered arrangement of double six-membered rings *d6r* (a.k.a. hexagonal prisms) and it covers ~45% of the surface, forming a two-dimensional percolated network. The remaining "uncovered" area leaves the Ru(0001) surface exposed through irregularly shaped holes of sizes in the mesopore scale range. The film morphology is different from that observed for pure silica, where a monolayer structure bound to the Ru substrate was produced under the same preparation conditions. The results provide further insights into the factors that influence the formation of two-dimensional frameworks intended to be used as model systems for surface science studies of rigid porous materials.

1. Introduction

The use of structure directing agents during the synthesis of zeolites is a well established method to tune the geometry of three-dimensional frameworks [1]. We have recently used a similar strategy to produce a two-dimensional framework. In that case, a flat metallic substrate was used as a template for the growth of a self-containing ordered aluminosilicate structure composed of a planar arrangement of hexagonal prisms, a.k.a. double 6-membered rings (*d6r*) [2]. A depiction of the structure is shown in Fig. 1b. A similar structure was reported before for a film containing only Si atoms in the tetrahedral positions [3]. In addition, a layered material called hexacelsian, reported as early as 1951 [4], also has this structure as a part of each layer. Interestingly, the structure of hexacelsian is also formed when the framework of the most widely used zeolite, Zeolite A, in its Ba-exchanged form, collapses upon thermal treatment [5]. Due to the nature of this new class of two-dimensional frameworks, the set of analytical tools used to characterize them is different from the ones commonly used to study zeolites and related materials. For example, diffraction patterns to assess the long range order of these films are obtained by low energy electron diffraction (LEED), instead of X-ray diffraction. The tools used to study these films belong to the field of surface science, for which a whole plethora of analytical techniques is available [6]. This offers the possibility of using the two-dimensional structures to perform very detailed studies on systems that share many properties with the three-dimensional zeolite analogs. For example, scanning tunneling microscopy (STM), allows the visualization of the structure down to the atomic scale [7] and it even offers the possibility of doing spectroscopy at the single atom level [8]. There is no doubt that studying structures to this level of detail translates into significant progress towards the understanding of zeolites, and other solid catalysts, and this has been made evident in recent years by the visualization of structures at the nanoscale using electron microscopies [9,10]. In addition, surface science studies allow the characterization of films in the extremely pristine conditions provided by ultra-high vacuum environments, down to 10^{-13} atm.

Needless to say, a significant difference of these films with three-dimensional zeolites is the lack of the rich variety of pores that are found in the latter. The only cavities present in the films are the small spaces contained within the hexagonal prisms and other, less frequently found, polygonal prisms [7]. However, the exposed surface of the film can be pictured as a pore of infinitely large size. In fact, we have demonstrated in a previous work that the same bridging hydroxyls found in acidic zeolites are present also in the two-dimensional films [2], and that they behave in a similar way towards the adsorption of probe molecules CO, C_2H_4, NH_3 and pyridine [11].

It was only recently that the preparation of silica and aluminosilicate ultra-thin films of well-defined structures was achieved [12]. Depending on the amount of Si and Al deposited during the

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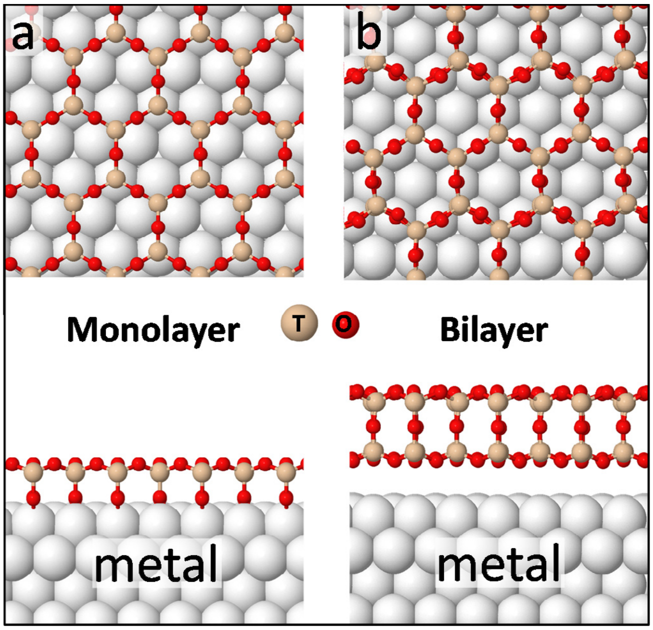

Fig. 1. Top and side views of (a) monolayer and (b) bilayer structures on a metal support. T stands for tetrahedral atoms (Si or Al).

film preparation, and the nature of the metallic substrate onto which the film was grown, it was found that monolayer or bilayer structures are produced. For clarity, we will now define a monolayer equivalent (MLE) as the amount of Si (or Al) necessary to produce the monolayer structure shown in Fig. 1a. Note that ordered structures for more than 2 MLE have not been reported yet.

While monolayer films are chemically bound to the metallic substrate through oxygen linkages Si—O—M [13], the bilayer case is a self-containing structure (all atoms are bound only to other atoms in the framework) in which the two layers are bound together by Si—O—Si(Al) linkages [3], and the interaction between the film and the substrate occurs through Van-der-Waals forces (see Fig. 1b). For example, for the case of crystalline silica films, only monolayers can be produced on Mo(112) [13] and only bilayers on Pt(111) [14]. For Ru(0001) both structures can be prepared depending on the amount of Si. Monolayers are obtained for 1 MLE of Si and bilayers are obtained for 2 MLE. Intermediate amounts of silicon give rise of films containing both monolayer and bilayer domains [15]. This was rationalized based on the affinity of oxygen to the metal support, which is reflected on the heats of dissociative adsorption of oxygen: Mo = –544 kJ/mol > Ru = –220 kJ/mol > Pt = –133 kJ/mol [14]. Since the Mo—O bond is so strong, a structure bound to the metal (monolayer) is thermodynamically more stable than one that is not (bilayer). The opposite is true for the Pt(111) case, for which the Pt—O bond is much weaker.

The aluminosilicate case is of prime importance to the zeolite community, since these films can be used to model some of the properties of zeolites using the versatile set of analytical tools available in surface science. On Mo(112) only monolayer films could be obtained and attempts to grow thicker ordered films were unsuccessful [16]. On Ru(0001), however, an aluminosilicate bilayer film consisting of SiO_4 and AlO_4^- tetrahedra was produced when 2 MLE of tetrahedral atoms T (Si or Al) were deposited [2,7]. Both of these cases are in agreement with what is expected from the results of silica films.

While the micropores in the zeolite structure play a major role in housing the active sites and in granting size selective access to small molecules, the importance of mesoporosity in the catalytic activity of zeolite crystals is increasingly being recognized. Recently, studies on H-ZSM-5 suggested that most of the activity in zeolite catalysts happens near the surface and the active sites in the interior of the individual crystals remains inaccessible to the reactants. Only severe steaming treatments generated extensive mesoporosity allowing the whole crystal to be accessible but at the cost of a significant loss in catalytic activity by depletion of active sites [17]. Since the presence of mesoporosity throughout the catalyst is beneficial to let bulky molecules go through to prevent blocking of the active sites, an alternative is the use of hierarchical zeolites which inherently contain mesopores in the structure, in addition to the micropores. An example of this is the use of three-dimensional arrangements of two-dimensional structures such as thin zeolite sheets to build more complex structures with channels in the mesopore scale [18].

In the present work we report a case in which 0.9 MLE of T atoms (Si + Al) are deposited on Ru(0001) which, based on what was found for silica, should form a monolayer structure. However, we find that a percolated network with bilayer structure covering half of the surface is formed. Interestingly, the percolated network leaves voids with sizes in the mesoporous scale range, through which the Ru(0001) template is exposed.

2. Experimental

All experiments reported here were performed in an ultrahigh-vacuum (UHV) system (base pressure ~5 × 10^{-10} mbar) counting with the following techniques: X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRAS), scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Silicon was deposited using an e-beam-assisted evaporator (Focus EFM3). During evaporation, the substrate was biased at the same potential as the Si rod (1000 V) to prevent acceleration of ions toward the sample, which could create uncontrolled defects. Aluminum was evaporated from a home-built evaporator consisting of a crucible containing metallic Al. The film was prepared on a Ru(0001) sample (10 mm in diameter and 1.5 mm in thickness from Mateck) surface which was first cleaned with cycles of Ar^+ sputtering (2 kV, 15 μA) and annealing to ~1200 °C. The clean surface was then pre-covered with a 3O-(2 × 2) overlayer by exposing the crystal to 3 × 10^{-6} mbar O_2 at 950 °C. The aluminosilicate film was prepared by subsequently depositing ~0.57 MLE of Si and ~0.33 MLE of Al on the 3O-(2 × 2)/Ru(0001) surface under an O_2 pressure of 2 × 10^{-7} mbar. 1 MLE is defined as the number of T atoms (Si or Al) necessary to make 1 ML of the structure shown in Fig. 1a. Note that 1 MLE corresponds to approximately 0.79 × 10^{15} T atoms/cm^2, this corresponds to 1 T atoms for every 2 Ru surface atoms. The composition of the film was confirmed by XPS. A correction factor of 1.17 was applied to the ratio of the peak areas Si 2p/Al 2s, based on previously reported experimental sensitivity factors [19]. This same procedure was followed in our previous articles and it accounts for the difference in cross section of Si 2p and Al 2s core levels [2,7,11]. The film was then oxidized by exposing it to a pressure of O_2 of 3 × 10^{-6} mbar while heating the sample up to ~950 °C, keeping it at this temperature for 10 min and then cooling it down always under O_2 ambient.

STM images were acquired with and Omicron ST Microscope at 300 K in the constant-current mode, with a current set-point of ~66 pA and bias voltage of –0.7 V applied to the sample. Image processing was done with WSXM software [20].

3. Results

Fig. 2a shows an STM image of the aluminosilicate film, where the area covered by the film can be clearly distinguished from the voids that leave the Ru(0001) surface exposed. The hexagonal