Spontaneous and artificial structures of thin, Keggin-like polyoxometallate arrays on graphite

I. Kovács
Institute of Isotopes, Department of Surface Chemistry and Catalysis, Hungarian Academy of Sciences, P. O. Box 77, H-1525 Budapest, Hungary

E-mail: kovacsi@sunserv.kfki.hu

Abstract. Scanning tunnelling microscopic studies have been performed to study the 2D structuring of the inorganic salt, the Keggin-type $\text{[AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}\text{]}^{7+}$ in its sulfate form. This compound forms patches of well ordered monolayer separated by defects seen on large scan images on the top of highly oriented pyrolitic graphite surface. A negative differential resistance peak has been found by scanning tunnelling spectroscopy. Surfactant molecules self-assemble horizontally in the first layer on the graphite plane. Higher uptake resulted in the formation of hemicylinders. In this study sodium dodecyl sulfate has been used to modify the 2D Keggin arrangements. By this combination of organic and inorganic materials the large counter ions were expected to re-arrange on the surface. In this surfactant assisted artificial ordering the distance between the Keggin-type units has been increased.

1. Introduction
The Keggin-like inorganic complex ions are common in polyoxometallate chemistry [1-3]. The characteristic dimension of such units is about 1 nm, both for cations and anions. Besides the academic interest these studies are of practical importance, too, such as preparation of pillared clay catalysts for shape selective processes or sensor applications [3-6]. Scanning Tunnelling Microscopic (STM) studies on thin, “monomolecular” layers of such compounds confirmed their two dimensional order [7]. These structures were very similar to the low index planes of the corresponding bulk crystals [1-3, 7-8]. Detailed studies on thin films of heteropoly acid derivatives revealed linear correlation between their scanning tunnelling spectroscopic (STS) characteristics (negative differential resistance, NDR ) and their catalytic activities [8,].

The so-called $\text{Al}_{13}$-Keggin ion, $\text{[AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}\text{]}^{7+}$ is a result of the forced partial hydrolysis of $\text{AlCl}_3$ solution. This polycation in the form of sulfate or selenate salt has a similar structure - named “$\text{Al}_{13}$-Keggin” - as the core anions of heteropoly acids. Studies on the chemistry of $\text{Al}_{13}$ became more interesting in the last decade due to its importance in catalytic and environmental applications [9-12]. It has been predicted by molecular mechanics simulations that no two dimensional ordering or any regular stacking of complex ions occur in the interlayer of pillared clays [11]. Up to now no STM or AFM studies have been published for $\text{Al}_{13}$-Keggin layers. We found that $\text{Al}_{13}$ Keggin ions in a thin, monomolecular layer are arranged in 2D structure on the graphite surface [12].
The goal of this work is to influence this “spontaneous order”, crystal structure and to prepare artificial arrangements by applying template molecules such as tensides and chelates. The AFM images of the adsorbate structure of the ionic surfactants, such as sodium dodecyl sulfate (SDS), suggested a two-step adsorption mechanism [13]. In the first adsorption step, the surfactant molecules self-assemble horizontally on the graphite plane, parallel to each other but in a head-to-head, tail-to-tail arrangement. In the second step, surface hemicylinders are formed in response to hydrophobic interactions between the exposed alkyl chains in the ordered monolayer and of the molecules in the bulk solution. Király et al. [13] have shown that their microcalorimetric study is fully consistent with current views - imaged by AFM - on surface aggregation at the solid/solution interface and that the mechanisms of cationic and anionic surfactant adsorption on graphite are very similar. The adsorption in the low-density adsorbate region is strongly exothermic and has been found to be nonreversible; only a fraction of the bound SDS monolayer can be removed in desorption steps, even on washing with pure water together with the less exothermic bound molecules which adsorbed in the second step. The polar end-groups of the molecules can form “lines” separated by the alkyl chains so it was expected to have guidelines for the next adsorption. For this purpose, we tried to use long chain alkyl and aryl derivatives. In this work only the results obtained with sodium dodecyl sulfate (SDS) will be shown.

2. Experimental

2.1. Materials and Preparations
The preparation of Al$_{13}$-Keggin-salt - Na[AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$][(SO$_4$)$_4$.10H$_2$O - has been previously described in detail [9]. The thin “Keggin-layer” for STM studies was prepared by droplet method [7].

The dry Keggin-salt was easily dissolved in 2x distilled water at room temperature at pH = 4.5. Then the HOPG was freshly cleaved and a few µ-liter of solution was filtered through a Milly-Q filter (<0.2 µm) and dropped onto it. Afterwards the sample was kept for 4 hours in air and the excess liquid was flushed. The sample was dried for 1 hour at 40 °C and then placed into the STM. After thermal equilibrium the sample was ready for STM or STS. In the second part of our work the freshly cleaved sample was first saturated by 80 mmol dm$^{-3}$ SDS solution. The excess of solvent was poured and the surface was washed by 150 mmol dm$^{-3}$ NaCl. After this removal – only the irreversibly bonded surfactant layer is on the surface – the 250 mmol dm$^{-3}$ Keggin-salt solution has been dropped on the surface as mentioned above.

2.2. Methods and Analysis
The STM studies were performed with an RHK-STM and STM-100 electronics. The images were collected at room temperature, under atmospheric pressure in air. Tips were freshly cut from a 0.1 mm diameter Pt/Ir wire Tunnelling conditions were for tip sample voltage between +0.3 V - -1.5 V and the current was between 0.1 nA - 1.5 nA. The images were collected in the topographic mode (constant current) STM spectroscopy (STS) was implemented at several locations, on the covered and on the clean HOPG surface. The sample voltage is then swept from –2 V to + 3 V, while recording the tunnelling current.

The crystallographic models were calculated with “Mercury, CCDC” program according to [14]. X-ray photoelectron spectroscopy was also performed to confirm the presence of Al$_{13}$ on the surface by an XSAM800 photoelectron spectrometer manufactured by KRATOS. Al K$_\alpha$ and Mg K$_\alpha$ characteristic X-ray lines and 80 eV or 40 eV pass energy were applied to measure the wide scan spectra and the characteristic Al, O, Na and S lines of our compound. We used both of the two different sources in order to confirm the validity of some peaks and in order to find better signal to noise condition. The BE values were Al 2p 74.8 eV, and O 1s 532.2 eV. The BE values obtained by XPS on Al$_{13}$ Keggin-salt powder were slightly different from the data in this work [15].
2.3. Computational details
We have performed density functional calculations, using B3LYP exchange-correlation functional. The preliminary runs employed 6-31G basis set, which is now being improved by polarization functions on the heavy atoms. We have done full geometry optimization on the [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]²⁺ cluster [12].

3. Results and Discussions

3.1. Spontaneous ordering
It can be seen on Figure 1A that Al₁₃-Keggin ions form a well ordered two dimensional order on graphite. The unit cell parameters are 1.4 nm x 0.95 nm with R=57°. The corresponding atomic arrangements – in Figure 1B - have been calculated by the program “Mercury” [14] based on the X-ray crystallographic data [9]. This layer is not regular on wide scan images, but it is decorated by defects as shown on Figure 1C. Considering the slightly higher than 1 monolayer coverage and the preparation irregularities breaking the long range order can be interpreted. Further exposures of this salt form column-like structures on the surface, Figure 1D, which might be related to the fiber shaped amorphous structure observed in bulk materials [16].

On a support, like graphite the ionic interactions and H-bonds stabilize the layer. The size of counter ions and water content determine the distance between more or less separated Al₁₃-Keggin units. By analogy – as in the case of Cs₂₅H₀₅PW₁₂O₄₀ catalyst [4] – such a layer might only absorb gases having small molecules.

Figure 1. Spontaneously ordered Al₁₃ units. Part A, a regular array (25 nm x 25 nm, 500 mV, 1.0 nA). Part B, the unit cell shown from the 110 direction. Part C, large scan view of the layer (300 nm x 300nm, 360 mV, 1.1 nA). Part D, columnar structure of Al₁₃-salt (125 nm x 125 nm, 2.0 V, 1.2 nA)

3.2. Artificial ordering
The adsorption of SDS on the graphite resulted in the formation of hemicylinders. After pouring off the liquid from the sample the surface showed a stripped structure, Figure 2A. According to our previous conception, the sample was washed with NaCl solution and only the irreversibly bonded monolayer is left on the surface, as shown in the scheme.

The surfactant oriented structuring during the adsorption of Keggin-salt on the pre-covered surface resulted in tiny lines as shown in Figure 2B and well ordered flat patches with an average mesh of 3.25 nm x 2.9 nm with R=90° (Figure 2C). A possible interpretation of these images is given in the inserts. The lack of densely packed parallel lines, which were expected, and the easily observed new, two dimensional structure suggests that this relaxed structure could be more stable, and the SDS-graphite interaction is feeble to keep the original structure. A proper selection of surfactant molecule would probably enhance the formation of regular, well separated, parallel oriented structures.
Figure 2. Part A, 3D view of SDS hemicylinders by STM (650 mV, 0.2 nA) and the scheme of the strongly bonded monolayer. Part B, formation of lines of Al$_{13}$-units (Part A, 500 mV, 1.1 nA). Part C, patches of separated Al$_{13}$-units (600 mV, 1.2 nA).

3.3. Spectroscopic studies
Scanning tunnelling spectroscopy over thin layers of Al$_{13}$-Keggin salt on graphite shows negative differential resistance (NDR) between +1.5 V and +2.5 V sample bias, and a ~4.0 eV broad band gap. Scanning at and above the NDR was not possible. This can be in accordance with the fact that the reproducibility of STS curves was poor.

Figure 3. Part A, The I-V spectra of Keggin-unit covered surface. Part B, Valence level structure of Keggin-sulphate measured by XPS, with corresponding molecular orbitals from DFT calculation.

Photoelectron spectroscopic (XPS) measurements were used not only to confirm the chemical composition of the surface but care was taken for detecting the valence band region. The top of the valence band was around 4.5 eV below the Fermi-edge with a broad band between 4.5 – 14 eV. The band gap cannot be determined by XPS alone, but it has to be larger then 4.5 eV. Although STS gives only 4.0 eV this is not antagonistic when taking into account the role of water which was certainly less under UHV conditions during XPS than in ambient air in STM/STS measurements. The B.E. values of the highest band in our spectra are very close to the values of other water free Al$_2$O$_3$ layers grown on Ni$_3$Al(111) in UHV [17]. The band gap of this oxide layer was estimated ~7 eV by UPS and STM.

Identifying the spectral features in XPS we performed DFT calculations. Careful analysis of the experimental and theoretical data will be given in detail [12]. Here we give a brief overview based on our preliminary DFT results. According to these calculations Al$_{13}$-Keggin ion has 4 eV broad band gap. The dense occurrence of bands below HOMO as well as above LUMO dense gives possibilities for different electron transitions in the layer. In the case of monolayer coverage we may also consider
another possible excitation mechanism, when the electron from the Fermi-edge of HOPG went to the LUMO bands. Similar to the surface assisted photochemical reaction, when an electron is transferred to the empty band and finally the molecule will decompose, see for example [18]. In the case of Al_{13}-Keggin salt on graphite the LUMO bands are located on O-H bonds of HO-H and O-H. The excited state may relax by a proton hopping from the given position to the STM tip or migrate inside the unit. Finally the H-bond network of the surface layer was destroyed, resulting in bad reproducibility in STS.

**4. Conclusions**

The Keggin-like inorganic, positively charged aluminium complex in the form of sulphate salt has a 3D structure which is isomorphous with hetero-polyacid anions. Thin, monomolecular layers of this compound can be prepared on graphite, HOPG surface and successfully imaged by STM. Our spectroscopic studies confirmed that the large amount of water and OH groups present in this layer, have influence on the electronic properties. By applying surfactant molecules it is possible to change the original arrangements of the Keggin units. This method opens a new way in preparation of pillared layered clay catalysts.

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**References**

[1] Keggin J F 1933 Nature (London) **131** 908
[2] Johansson G 1960 Acta Chem. Scand. **14** 771
[3] Mizuno N and Misono M 1998 Heterogeneous Catalysis Chem. Rev. **98** 199
[4] Okuhara T 2003 Appl. Catal. A: General **256** 213
[5] Pálinkó I, Molnár Á, Nagy J B, Bertrand J-C, Lázár K, Valyon J and Kiricsi I 1997 J. Chem. Soc. Faraday Trans., **93** 1591
[6] Comuzzi C, Dolcetti G, Trovarelli A, Cavani F, Trifiro F, Lorca and Finke R G 1996 Catal. Lett. **36** 75
[7] Barteau M A, Lyons J E and Song I K 2003 J. Catal. **216** 236
[8] Song I K and Barteau M 2004 A Langmuir **20** 1850
[9] Parker W O Jr., Millini R and Kiricsi I 1997 Inorg. Chem. **36** 571
[10] Casey W H 2006 Chem. Rev. **106** 1
[11] Čapková P, Driessen R A J, Schenk H and Weiss Z 1997 J. Mol. Model. **3**, 467
[12] Kovács I, Kiricsi I, Schay Z and Stirling A in preparation
[13] Király Z, Findenegg H, Klumpp E, Schlimper H and Dékány I 2001 Langmuir **17** 2420
[14] Mercury 1.3 Copyright CCDC 2001-2004 http://www.ccdc.cam.ac.uk/mercury/
[15] Oszkó A, Kiss J and Kiricsi I 1999 Phys. Chem. Chem. Phys. **1** 2665
[16] Wanga M and Muhammed M 1999 Nanostructured Materials **11** 1219
[17] Rosenhahn A, Schneider J, Kandler J, Becker C and Wandelt K 1999 Surf. Sci. **433-435** 705
[18] Kovács I, Iost N and Solymosi F 1994 J. Chem. Phys. **101** 4236