

Acid-Basic Site Detection and Mapping on Solid Surfaces at the Nanoscale, by Kelvin Force Microscopy (KFM)

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ABSTRACT

Nanoscale electric potential patterns of acid and basic solid surfaces is modified under variable relative humidity, as determined by using Kelvin force microscopy (KFM). The electrostatic potential on acid surfaces becomes more negative as the water vapor pressure increases, while it becomes more positive on basic solids. These results verify the following hypothesis: OH⁻ or H⁺ ions associated with atmospheric water ion clusters are selectively adsorbed on solid surfaces, depending on the respective Brønsted acid or base character. KFM under variable humidity is thus a rigorous but convenient alternative to determine acid-base character of solid surfaces at the nanoscale, thus contributing to detailed knowledge of particulate matter, which is currently inaccessible to any other method.

Keywords: Kelvin force microscopy, Brønsted acid-base, solid surfaces, nanoscale and relative humidity.

1. INTRODUCTION

Adsorptive and catalytic properties of acid and basic solids, such as zeolites oxides, salts and sulfonated polymers are decisive in many industrial processes [1,2]. The concentration and strength of acid and basic sites influence their surface activity. However, due to the complexity of solid catalyst chemical structures and the large number of synthetic relevant variables, current techniques are not sufficient to elucidate conflicting results in the literature [3]. Besides, these techniques are macroscopic, giving overall data for each sample, but not providing information on the spacial distribution of acid-base sites on surface. The present work reveals that the electric potential pattern of acid and basic solid surfaces, measured by Kelvin force microscopy (KFM), is altered under variable relative humidity [4].

2. EXPERIMENTAL SECTION

2.1 Samples

Amorphous aluminum phosphate is a developmental product supplied by Bunge [5]. Silica particles were prepared by the method of Stöber et al [6]. Aluminum, iron and nickel-iron alloy sheet surfaces of thickness 0.27, 1.22 and 0.65 mm respectively. Cellulose fibers were dispersed from Whatman quantitative filter paper 40, ashless grade. Magnesium oxide from Carlo Erba were used without further treatment. Calcium oxide supplied by Nuclear was calcined at 900° C for 90 minutes prior to use [4].

2.2 Atomic Force Microscopy (AFM) and Kelvin Force Microscopy (KFM)

Dry samples were imaged by atomic force microscopy (AFM) in Kelvin (electric potential) force mode (KFM), yielding topography and electric potential maps simultaneously, from the same surface area. Images were obtained in a Shimadzu SPM 9600 microscope using a Pt-coated silicon nitride cantilever (EFM-20 Nanoworld) with 75 ± 5 kHz resonance frequency and 2.9 ± 0.3 N/m spring constant. The microscope is fully contained within an environmental chamber that allows control of temperature, relative humidity, ambient pressure and atmosphere composition. Images were acquired under different RH conditions at 25°C.

The KFM technique uses the standard noncontact AFM setup. An AC signal is fed 10-20 kHz below the frequency of the normal AFM oscillator, which matches the natural frequency of mechanical oscillation of the cantilever-tip system (40-70 kHz). The principle is analogous to the Kelvin method, [7] except that forces are measured instead of current. The image is built using the DC voltage fed to the tip, at every pixel, thus detecting electric potential gradients throughout the scanned area.

3. RESULTS AND DISCUSSION

Kelvin force microscopy (KFM) measurements on acidic or basic solid surfaces reveal that electrostatic potential patterns change as the relative humidity (RH) varies within a grounded environment. Figure 1 presents topographic and KFM images of aluminum oxide on aluminum metal images at variable relative humidity. Electric potential-versus-distance linescans, extracted from the KFM micrographs, are shown in Figure 2. The overall initial sample potential is negative and when the humidity is increased to 70% RH, the electrostatic potential becomes even more negative (the average potential difference is -100 mV). For aluminum oxide surface, OH^- ions are adsorbed to a greater extent than H^+ ions from the water vapor, as expected, considering the acidic character of this surface, which is well-established in the catalysis literature [1].

Qualitatively similar results are verified for iron oxide on iron metal, silica, magnesium sulfate and cellulose, but there are quantitative differences due to the different chemical nature of these surfaces. The electric potential profiles are shown in Figure 3 for these acid surfaces.

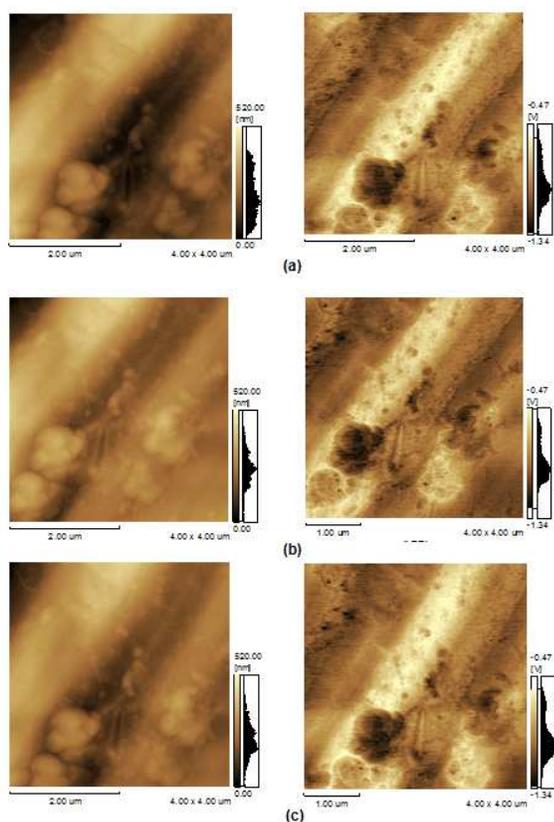


Figure 1: Topographic (left) and Kelvin force microscopy (KFM) (right) images from the same area of aluminum oxide on aluminum metal. Successive changes in the relative humidity were made prior to image acquisition: (a) 30% RH; (b) 70% RH and (c) back to 30% RH.

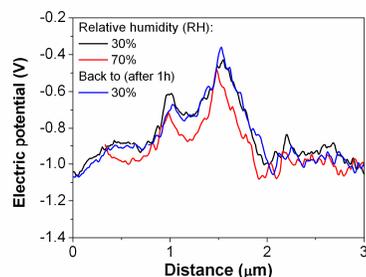


Figure 2: Linescans from the three consecutive KFM images of aluminum oxide on aluminum metal surface.

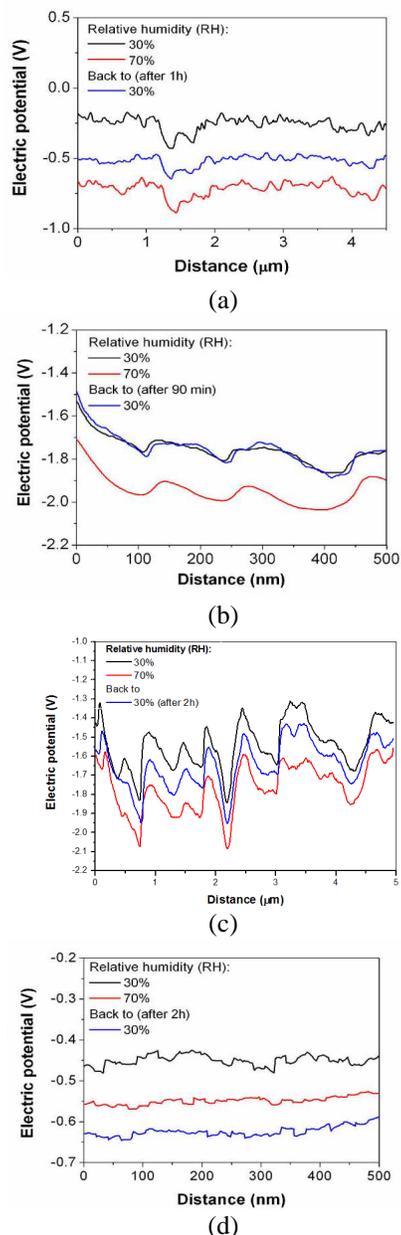


Figure 3: Linescans from four consecutive KFM images obtained at 30, 70 and 30% RH (a) iron oxide on iron metal, (b) silica (c) magnesium sulfate and (d) cellulose. The observed changes are at least partly reversible, except in the case of cellulose.

The electric potential on basic surfaces becomes more positive as the water vapor pressure increases as shown in Figures 4 and 5 for magnesium oxide surface. When the relative humidity raises from 30 to 70% RH, the magnesium oxide solid surface becomes less negative. However, when the humidity returns to 30% RH, this solid surface presents an irreversible behavior, which is explained considering the irreversibility of hydration reactions, under the conditions used in these experiments. Besides, AFM pictures also show irreversible changes in the magnesium oxide morphology, in agreement with previous results [8].

A remarkable feature is the smoothing-out of the potential vs. distance plots obtained after magnesium oxide was exposed to a higher relative humidity: the large local potential variations disappear, evidencing that some surface sites pick up H^+ ions from the atmosphere more pronouncedly than others and also that ions can migrate across the surface, reaching a more uniform charge density.

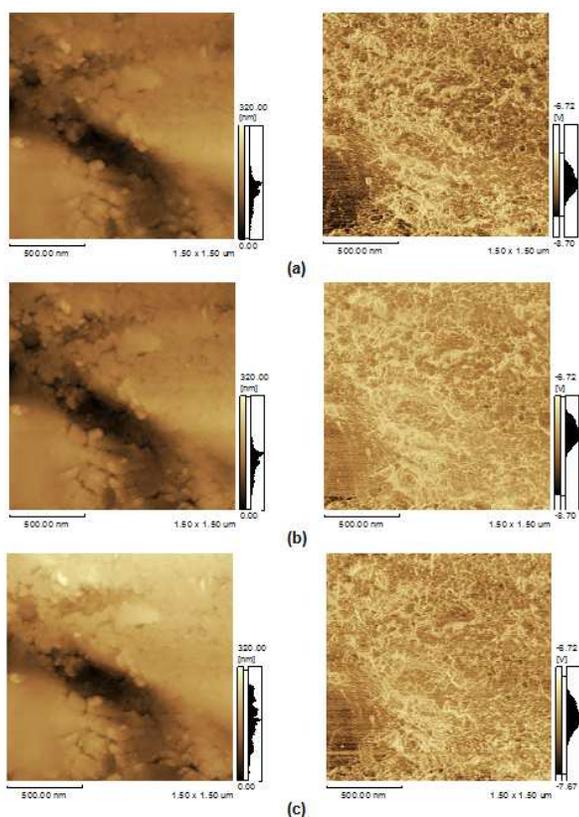


Figure 4: Topographic (left) and Kelvin force microscopy (KFM) (right) images from the same area of magnesium oxide. Successive changes in the relative humidity were made prior to image acquisition: (a) 30% RH; (b) 50% RH and (c) back to 30% RH.

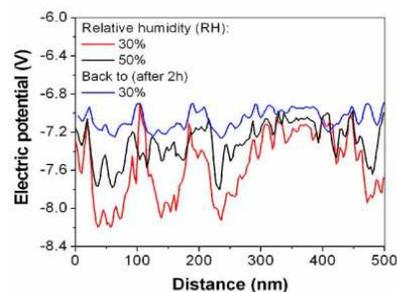


Figure 5: Linescans from the three consecutive KFM images of magnesium oxide.

Qualitatively similar behavior is observed on three other basic solids: nickel oxide on nickel-iron alloy, calcium oxide and noncrystalline aluminum phosphate, but with some quantitative differences, as shown in Figure 6. The observed changes are at least partly reversible, except in the case of magnesium oxide (Figure 5), because of the formation of a paste due to excessive water adsorption.

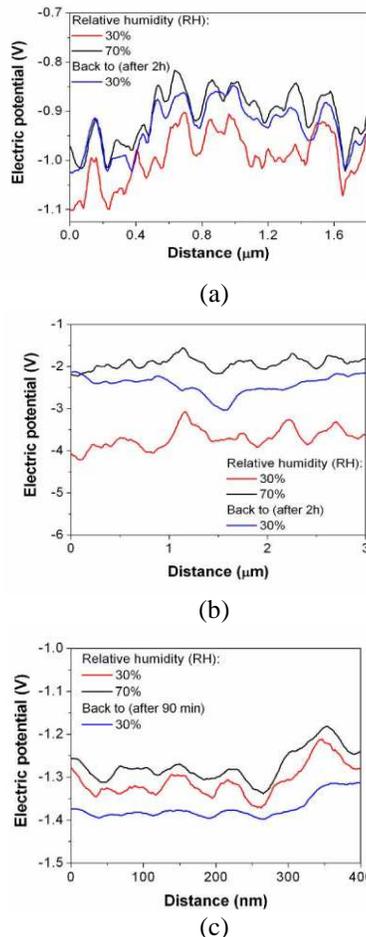


Figure 6: Linescans from three consecutive KFM images obtained at 30, 70 and 30% RH (a) nickel oxide on nickel-iron alloy, (b) calcium oxide and noncrystalline aluminum phosphate. The observed changes are at least partly reversible.

For a general overview, Table 1 shows the averaged and the calculated values for all the analysed samples. The average of the electrostatic potential variation (ΔV_m) was calculated as follows: linescans obtained at 30% and 70% RH were subtracted from each other, yielding a surface potential difference for each pixel.

Considering our current work hypothesis that H^+ and OH^- ions are partitioned between the solid surface and adsorbed water, depending on the Brønsted acid or base character of the surface, it is possible to assume that when the average of the electrostatic variation (ΔV_m) is negative, preferential OH^- adsorption takes place and thus the solid is an acid. On the other hand, positive average of the electrostatic variation is due to preferential H^+ adsorption and the solid is a base.

| Compound | ΔV_m | Character of the surface |
|--------------------|--------------------|--------------------------|
| Iron oxide | -0.464 ± 0.004 | Acid |
| Magnesium sulfate | -0.229 ± 0.008 | Acid |
| Silica | -0.172 ± 0.015 | Acid |
| Cellulose | -0.104 ± 0.007 | Acid |
| Aluminum oxide | -0.055 ± 0.016 | Acid |
| Calcium oxide | $+1.657 \pm 0.115$ | Base |
| Magnesium oxide | $+0.195 \pm 0.062$ | Base |
| Nickel oxide | $+0.060 \pm 0.017$ | Base |
| Aluminum phosphate | $+0.039 \pm 0.007$ | Base |

Table 1: Average electrostatic potential variation (ΔV_m) for the analysed solids, following an increase in humidity (from 30% to 70%).

4. CONCLUSIONS

Kelvin force microscopy under variable relative humidity is powerful, sensitive and convenient method to determine the acid-base characteristics of solids used as catalysts and adsorbents, with a great advantage: it uses only one amphoteric and simple reagent, that is water vapor. Furthermore, KFM provides information on the uniformity of the surface acid-base sites and also on their spatial distribution at nanoscale, thus contributing to detailed knowledge of particulate matter, which is currently inaccessible to any other method. Experiments can be done under various pressure and temperature conditions and also under variable atmosphere composition, thus this technique

can be largely exploited for studying acid-base catalysts and for in-situ study of catalytic reactions.

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