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# A density functional study of water and methanol chemisorption on MgO(1 1 0)

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## Abstract

Periodic density functional calculations have been used to study the adsorption of water and methanol on the (1 1 0) surface of MgO. A brief re-investigation of the (1 0 0) surface confirms previous results that the dissociative adsorption of $H_2O$ on MgO(1 0 0) is energetically unfavourable. We find the same to be true of $CH_3OH$. On the (1 1 0) surface, both water and methanol are strongly adsorbed, with high energies of adsorption. Water is dissociatively adsorbed with $\Delta E$ ranging from −290 kJ/mol at low coverage to −240 kJ/mol at a full monolayer. The adsorption of water is found not to be activated. $\Delta E$ for adsorption of methanol ranges from −255 to −240 kJ/mol. A mixed water–methanol adsorption layer is also possible, with a similar binding energy.

*Keywords:* Magnesium oxide; MgO(1 1 0); MgO(1 0 0); Water adsorption; Methanol adsorption; DFT calculation

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## 1. Introduction

Powdered magnesium oxide is commonly prepared by decomposition of a precursor compound, typically $Mg(OH)_2$, under vacuum at temperatures of the order of 500 K. Such a preparation yields a product with a specific surface area of a few hundred $m^2$ per gram, possessing a layer of surface hydroxyl groups whose concentration can be determined gravimetrically [1,2]. In the absence of high temperature treatment, the total concentration of hydroxyl groups corresponds to dissociative adsorption of 10–11$H_2O$ molecules per $nm^2$. This is close to the concentration of MgO units on a (1 0 0) surface, which is 11.2 per $nm^2$. Thus it has commonly been assumed that the powder preparations consist mostly of fully-hydroxylated {1 0 0}

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surfaces. The concentration of surface hydroxyls can be reduced by high temperature vacuum treatment. Prolonged pumping at 700 K will reduce the concentration to half its original value, while temperatures above 1000 K are required to effect complete removal of hydroxyls.

Several workers have studied MgO powders by electron microscopy. The most conclusive results involve MgO smokes produced by gas-phase oxidation of elemental Mg. These studies [3–5] clearly show the presence of MgO cubes, and hence (1 0 0) faces are dominant for samples prepared in this manner. The situation is much less clear for samples prepared by decomposition of the hydroxide [1] or basic carbonate [4], and it is difficult to draw any conclusions from the published micrographs. One group [6] reports (1 0 0), (1 1 1), (1 1 0), (2 1 0) and (2 1 1) facets on commercial MgO powders of unknown preparation. These workers report that (1 1 0) becomes the dominant orientation after high temperature treatment; since micrographs are not shown in this paper, it is difficult to assess the correctness of this assertion. It is interesting to note that Coluccia et al. [5] find cubic MgO smoke particles to be attacked by $H_2O$ vapour, with development of new faces. Thus it may well be the case that samples of MgO prepared in a water-containing environment (e.g. by hydroxide decomposition) expose planes other than the (1 0 0) surfaces found in smokes.

Infrared spectroscopy of powdered MgO preparations shows only OH stretching vibrations, with no evidence of a bending mode that would be characteristic of intact $H_2O$ molecules [2,7]. Bending modes are of course seen in the presence of physisorbed water at low temperatures, but are completely removed by vacuum treatment above 450 K. Proton NMR spectroscopy [8] shows a single broad line, with a second moment of $4.5\ \mathrm{G}^2$, consistent with the hydroxyl density of a fully hydroxylated (1 0 0) surface.

The simple view that the hydroxylated MgO surface exposes (1 0 0) planes is inconsistent with recent high-quality theoretical calculations. Scamehorn et al. [9] performed a periodic Hartree–Fock calculation with a posteriori correlation corrections, and found the dissociative adsorption of $H_2O$ on MgO(1 0 0) to be endothermic. The numerical values depend somewhat on the basis set and correlation functional used, but it appears that the endothermicity is at least 30 kJ/mol. In a subsequent paper [10] it was shown that model defects exposing edge and corner sites can lead to exothermic dissociative adsorption, but it is difficult to postulate edges and corners as a means to achieve essentially full monolayer coverage. Assuming cubes bounded by {1 0 0} surfaces, a typical specific area of $200\ \mathrm{m}^2\ \mathrm{g}^{-1}$ corresponds to an edge length of 84 Å. Such a cube has only 5% of its surface atoms on corners and edges.

It is known [11,12] that there are possible exothermic structures involving mixtures of dissociated and undissociated $H_2O$ on MgO(1 0 0), for example a c[$3 \times 2$] structure containing six water molecules, of which two are dissociated. Such structures cannot account for the experimental facts, since a bending vibration would be expected for the undissociated molecules, and the predicted energy of adsorption is only −46 kJ/mol, which would not lead to a stable layer at the temperature of preparation of MgO powders (see discussion below).

Hydroxylation has also been studied on the (1 1 1) surface. MgO(1 1 1) surfaces are polar, so planes containing only Mg are exposed on one side of the crystal, and planes with only O on the other. Such crystals possess a macroscopic electric dipole moment, which will render them unstable, in the absence of stabilizing surface structures. It is known that the (1 1 1) surface can be stabilized either by reconstruction [13] or by hydroxylation with complete layers of $OH^-$ and $H^+$ on the Mg and O surfaces, respectively [13,14]. Since stabilization requires complete layers of $OH^-$ and $H^+$, thermal dehydroxylation of the (1 1 1) surface must imply reconstruction, which might be expected to occur at relatively high temperatures. It is quite conceivable that powdered MgO may contain a substantial amount of (1 1 1) surface. This could account for the difficulty of dehydroxylation, and the slow rehydroxylation of dehydrated powders. Because of the higher site density on (1 1 1), a NMR second moment of $6.5\ \mathrm{G}^2$ is predicted, which is moderately at variance with the experimental results. It thus appears that neither (1 0 0) nor (1 1 1) surfaces can fully account for all experimental data on MgO powders. One can therefore