Vanadium oxide films on Au(111): model catalysts for methanol oxidation

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Vanadium oxide monolayers supported on metal oxides are an important class of catalysts for oxidation of methanol to formaldehyde. Although these catalysts are widely used in industry, little knowledge exists on the fundamentals of the oxidation of methanol on vanadium oxide surfaces. In order to circumvent experimental difficulties associated with the preparation of and measurements on oxide single crystals, well ordered films of V_2O_3(0001) and V_2O_5(001) were grown on a Au(111) single crystal. For the V_2O_5 film the thermal stability was carefully investigated. After deposition, V_2O_3 and V_2O_5 films are terminated with vanadyl (V=O) groups, which may be removed by electron bombardment. The reactivity of the films was probed by Temperature Programmed Desorption of methanol. Fully oxidised films were found to be unreactive for formaldehyde production, only (partially) reduced surfaces are active. The presence of vanadyl groups appeared to be essential for selectivity towards formaldehyde production. Scanning Tunnelling Microscopy (STM) studies showed that a nearly full coverage of methoxy species on V_2O_3 can be achieved, whereas the coverage on V_2O_5 is considerably lower. STM showed that on V_2O_5 mainly single vanadyl vacancies adsorb methoxy, moreover the available adsorption sites are only partially covered. X-ray Photoelectron Spectroscopy shows that this partial coverage is most likely explained by recombination of methoxy and hydroxyl groups, leading to desorption of methanol.