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Journal of Electron Spectroscopy and Related Phenomena 144–147 (2005) 377–380

JOURNAL OF ELECTRON SPECTROSCOPY and Related Phenomena

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UPS study of the thermal reduction of fully oxidized $V_2O_5/TiO_2(0\,0\,1)$-anatase model catalysts

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Abstract

The thermal reduction of thin vanadium oxide layers (8 and 16 Å) deposited with magnetron sputtering on mineral anatase $TiO_2(0\,0\,1)$ was examined with ultraviolet photoelectron spectroscopy (UPS). Completely oxidized vanadium oxide layers were deposited. During heating, the vanadium oxide layers reduced and evaporated, the thinnest vanadium oxide layer (8 Å) even vanished. A re-oxidation of the heated 16 Å V_2O_5/TiO_2 could not restore the reduced vanadium oxide completely to V^{5+}.

Keywords: Photoelectron spectroscopy; UPS; Supported vanadium oxide; TiO_2 anatase; Model catalyst

1. Introduction

The supported V_2O_5/TiO_2 (anatase) system is an important catalyst for the selective oxidation of hydrocarbons [1].

To study the V_2O_5/TiO_2 (anatase) system we have developed a model catalyst composed of a vanadium oxide layer deposited on mineral single crystal anatase $TiO_2(0\,0\,1)$. As industrial V_2O_5/TiO_2 (anatase) catalysts are calcined or activated before use in reaction and contain mostly V^{5+}, representative model catalysts should also have fully oxidized vanadium oxide layers, which were obtained previously [2]. We have studied the thermal reduction of 8 and 16 Å V_2O_5 layers on anatase $TiO_2(0\,0\,1)$ with synchrotron UPS.

2. Experimental

Mineral anatase single crystals are used. The crystals are Laue-oriented and sawn to the (0 0 1) surface and polished with Al_2O_3 powder with a grain size down to 0.3 μm. The $\sim 15\,mm^2$ TiO_2 substrates are ultrasonically cleaned in ethanol before introduction into UHV. Two slices from the same crystal are used.

All experiments are performed at the SA73 beamline of the S.ACO storage ring (LURE). The anatase surfaces are cleaned by Ar^+ bombardment (8.5×10^{-3} Pa, 580 eV, 30 min, 0.5–2.71 μA) followed by annealing in O_2 (2.5×10^{-1} Pa, 60 min, 300–320 °C). The vanadium oxide layers are deposited with reactive dc magnetron sputtering [3] from a 2 in. polycrystalline V_2O_5 target in O_2 (1 Pa, 8.2 sccm flow O_2) at constant power (50 W, discharge voltage: 430 V). The deposition rate is 2 Å/min. Two model catalysts are deposited: 8 and 16 Å V_2O_5.

A Si plane grating (500 lines/mm) is used as monochromator. The photoelectron intensity along the sample normal is detected with a hemispherical analyser (EA 125, Omicron, 5 channeltrons). V3p, Ti3p, O2s and valence band (VB) spectra are recorded with an excitation energy of 150 eV, an energy step of 0.1 eV and a resolution of 0.125 eV (pass energy = 20 eV). The binding energy (BE) scale is calibrated with a Au sample. During heating, spectra are taken with an energy step of 0.2 eV and a resolution of 0.2 eV (pass energy = 32 eV). Heat treatments are performed in situ in the

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doi:10.1016/j.elspec.2005.01.020

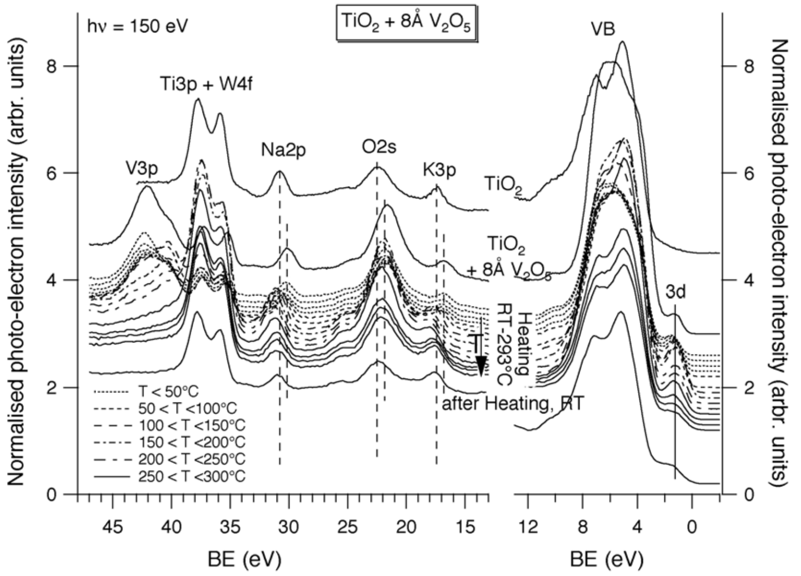

Fig. 1. UPS measurements for 8 Å V_2O_5/TiO_2. A temperature legend for the spectra during heating is given.

main chamber. Temperatures are determined with an AlCr thermocouple in contact with the sample holder. The 8 Å V_2O_5/TiO_2 is heated from room temperature (RT) to 293 °C and the 16 Å V_2O_5/TiO_2 to 242 °C.

A re-oxidation is given to 16 Å V_2O_5/TiO_2 after the heat treatment by annealing to 150 °C in 5×10^{-1} Pa O_2 (60 min). UPS spectra are normalized according to Kurtz et al. [4].

3. Results and discussion

UPS spectra for 8 Å V_2O_5/TiO_2 and 16 Å V_2O_5/TiO_2 are given in Figs. 1 and 2, respectively. The anatase TiO_2(0 0 1) substrate spectra contain Ti3p (37.3 eV), O2s (22.2 eV) and VB (3–9 eV), and also Al2p (around 74.5 eV, not shown), Na2p (31.0 eV) and K3p (17.4 eV, the weaker K3s around 34.0 eV). The peak around 10–11 eV are the 3σ orbitals of OH adsorbed on anatase [5,6].

The substrate for 8 Å V_2O_5/TiO_2 contains also a W4f doublet (37.9 and 35.8 eV) coinciding with the Ti3p. A deconvolution example is given in Fig. 3. These contaminants are naturally present in the anatase, the Al originates from the Al_2O_3 polishing powder. Since the photoionization cross section for W4f and Na2p are higher than for V3p and Ti3p [7], the contaminant signals are relatively intense.

The deposition of vanadium oxide shifts all core levels and the VB to lower BE by about 0.8 eV, due to a work function change of the surface. The VB spectra for the thin

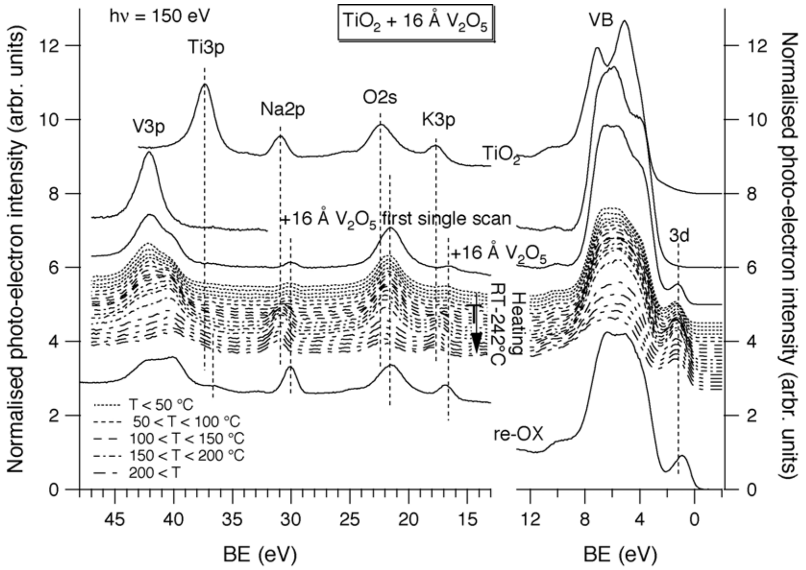

Fig. 2. UPS measurements for 16 Å V_2O_5/TiO_2. A temperature legend for the spectra during heating is given.