Supplementary information to:

Mechanistic Studies of Atomic Layer Deposition on Oxidation Catalysts – AlO_x and PO_x Deposition

Kristian Knemeyer,[a] Mar Piernavieja Hermida,[a] Piyush Ingale,[a] Johannes Schmidt,[b] Jutta Kröhnert,[c] Raoul Naumann d'Alnoncourt,*[a] Matthias Driess,[a,b] and Frank Rosowski [a,d]

[a.] *BasCat—UniCat BASF JointLab, Technische Universität Berlin, Hardenbergstraße 36, 10623 Berlin, Germany. *E-mail: r.naumann@bascat.tu-berlin.de*
[b.] *Institut für Chemie, Technische Universität Berlin, Straße des 17, Juni 135, 10623 Berlin, Germany.*
[c.] *Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany.*
[d.] *BASF SE, Process Research and Chemical Engineering, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany.*

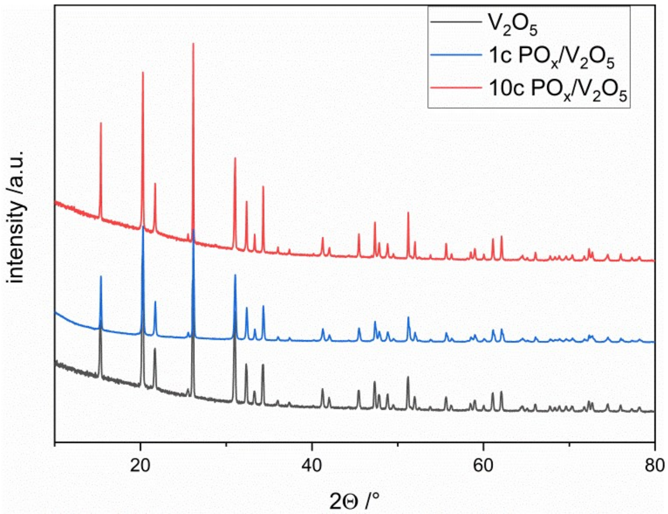

Fig. 1 XRD of V_2O_5, 1cycle PO_x-ALD and 10 cycle PO_x-ALD on V_2O_5. Reflexes were exclusively found which can be assigned to vanadium pentoxide. No additional reflexes found in phosphorus system.

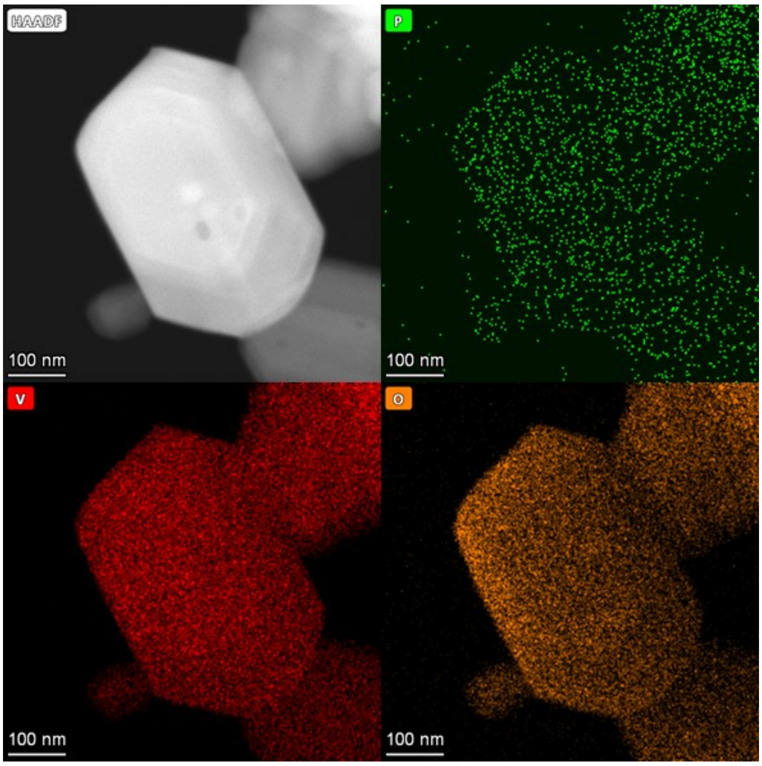

Fig. 2 HAADF image of PO_x/V_2O_5 prepared by 1 cycle of PO_x-ALD and STEM-EDX mappings of P, V and O.

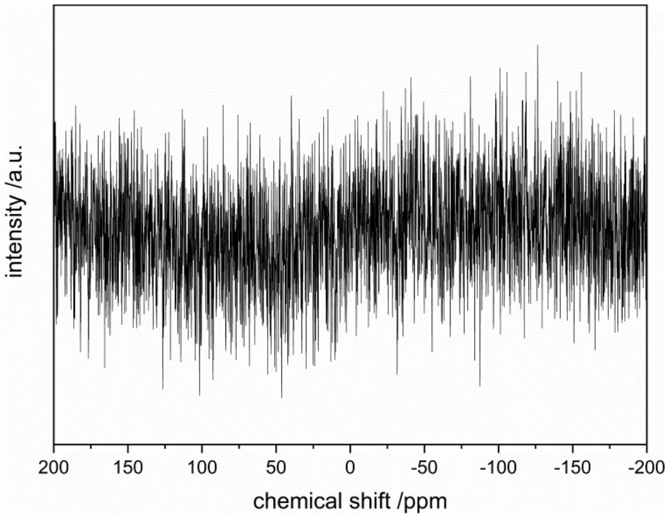

Fig. 3 ^{31}P-NMR after first half cycle of TMPT dosing on V_2O_5 at 150 °C. No P Signal is obtained.

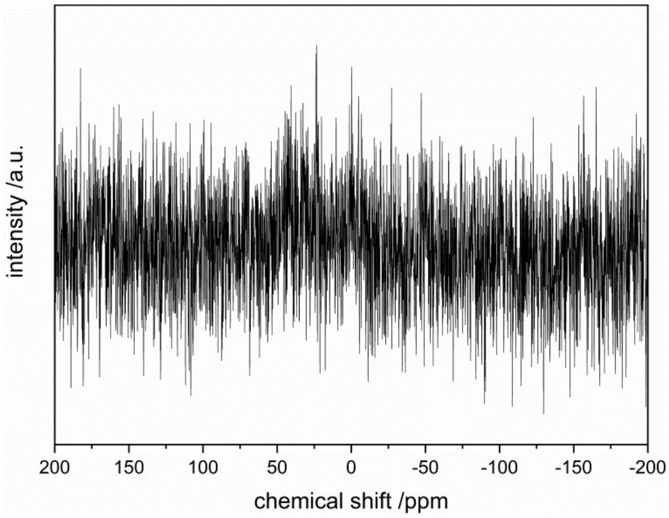

Fig. 4 [31]P-NMR after first cycle of TMPT dosing on V_2O_5 with subsequent oxygen dosing at 150 °C. No P Signal is obtained.

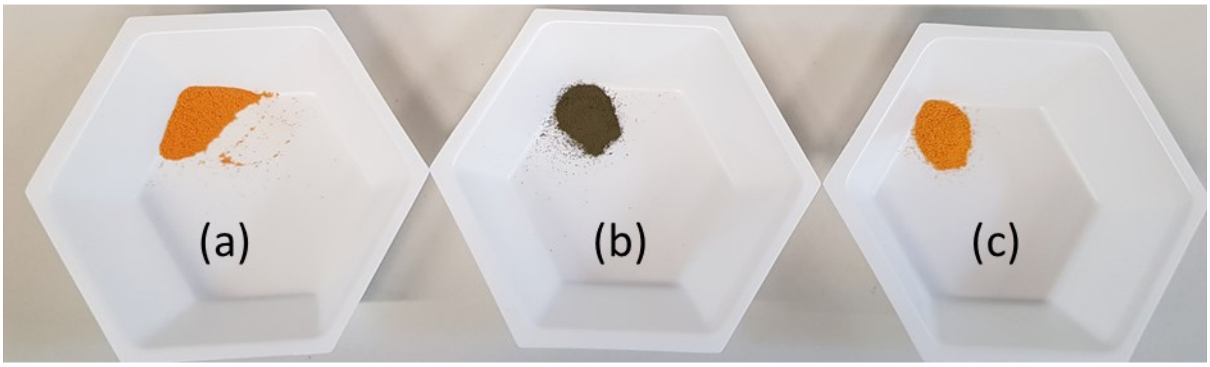

Fig. 5 (a) V_2O_5 before ALD, (b) after exposure to one half cycle of TMPT at 150 °C, (c) after one cycle of TMPT at 150 °C and oxygen at 450 °C. The color changes from orange to green in the first half cycle and from green to orange after the second half cycle.

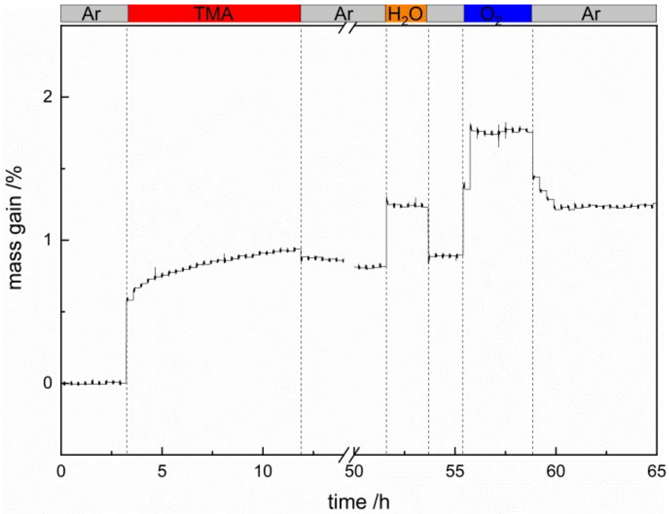

Fig. 6 Mass gain in magnetic suspension balance for reaction sequence $TMA/H_2O/O_2$ with TMA and water dosing at 150 °C and O_2 dosing at 450 °C.

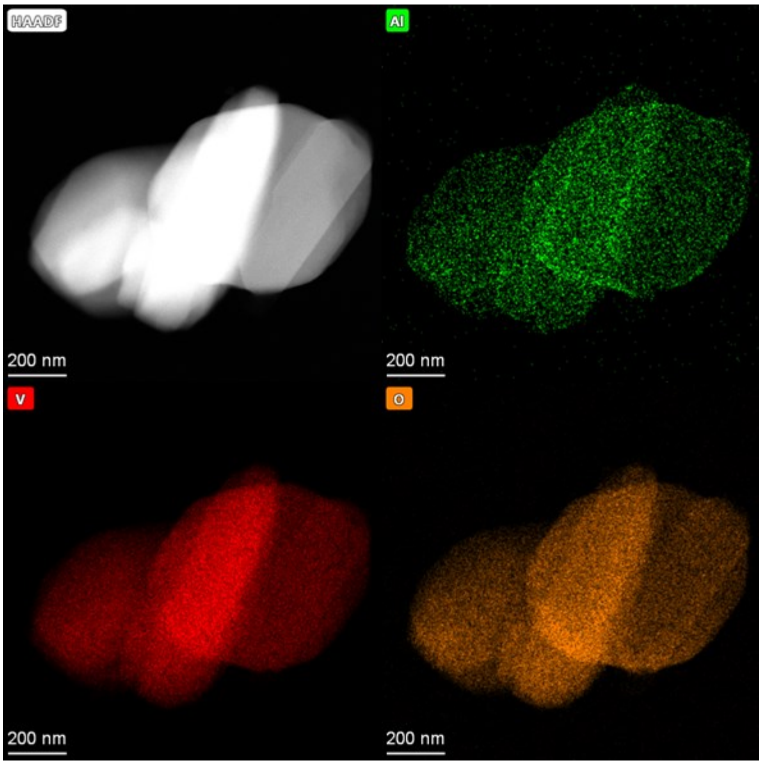

Fig. 7 HAADF image of AlO_x/V_2O_5 prepared by 1 cycle of AlO_x-ALD and STEM-EDX mappings of Al, V and O.

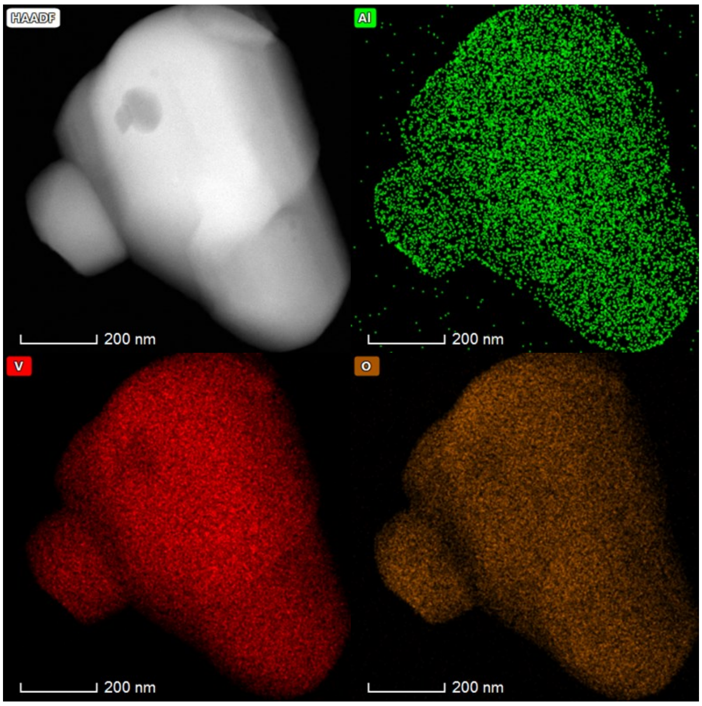

Fig. 8 HAADF image of AlO_x/V_2O_5 prepared by 6 cycles of AlO_x-ALD and STEM-EDX mappings of Al, V and O.

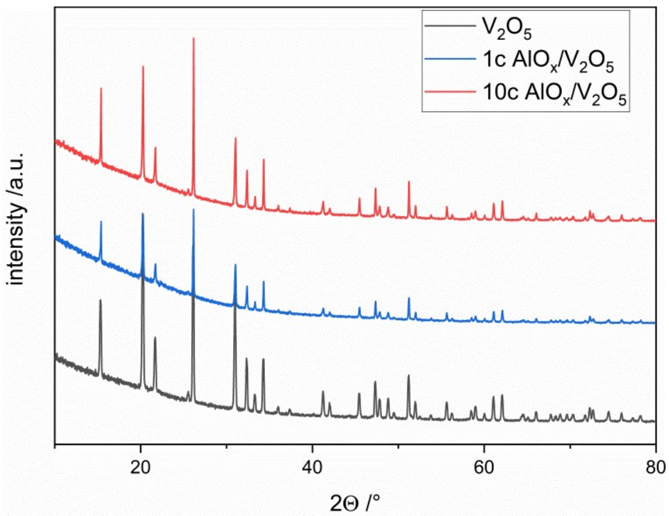

Fig. 9 XRD of V_2O_5, 1cycle AlO_x-ALD and 6 cycle AlO_x-ALD on V_2O_5. Reflexes were exclusively found which can be assigned to vanadium pentoxide. No additional reflexes found in aluminum system.

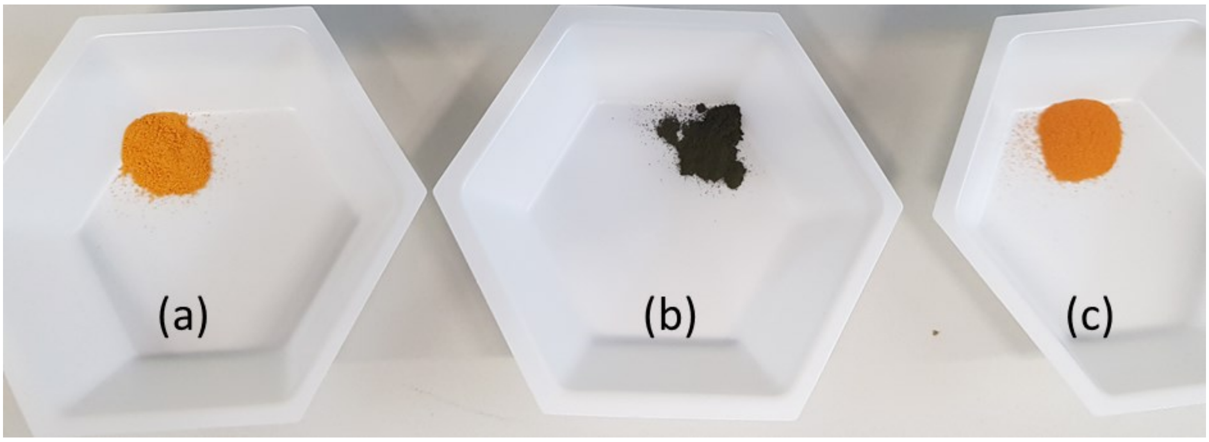

Fig. 10 (a) V_2O_5 before ALD, (b) after exposure to one half cycle of TMA at 150 °C, (c) after one cycle of TMA and water at 150 °C and subsequent thermal treatment in oxygen at 450 °C. The color changes from orange to green in the first half cycle and from green to orange after the thermal treatment.

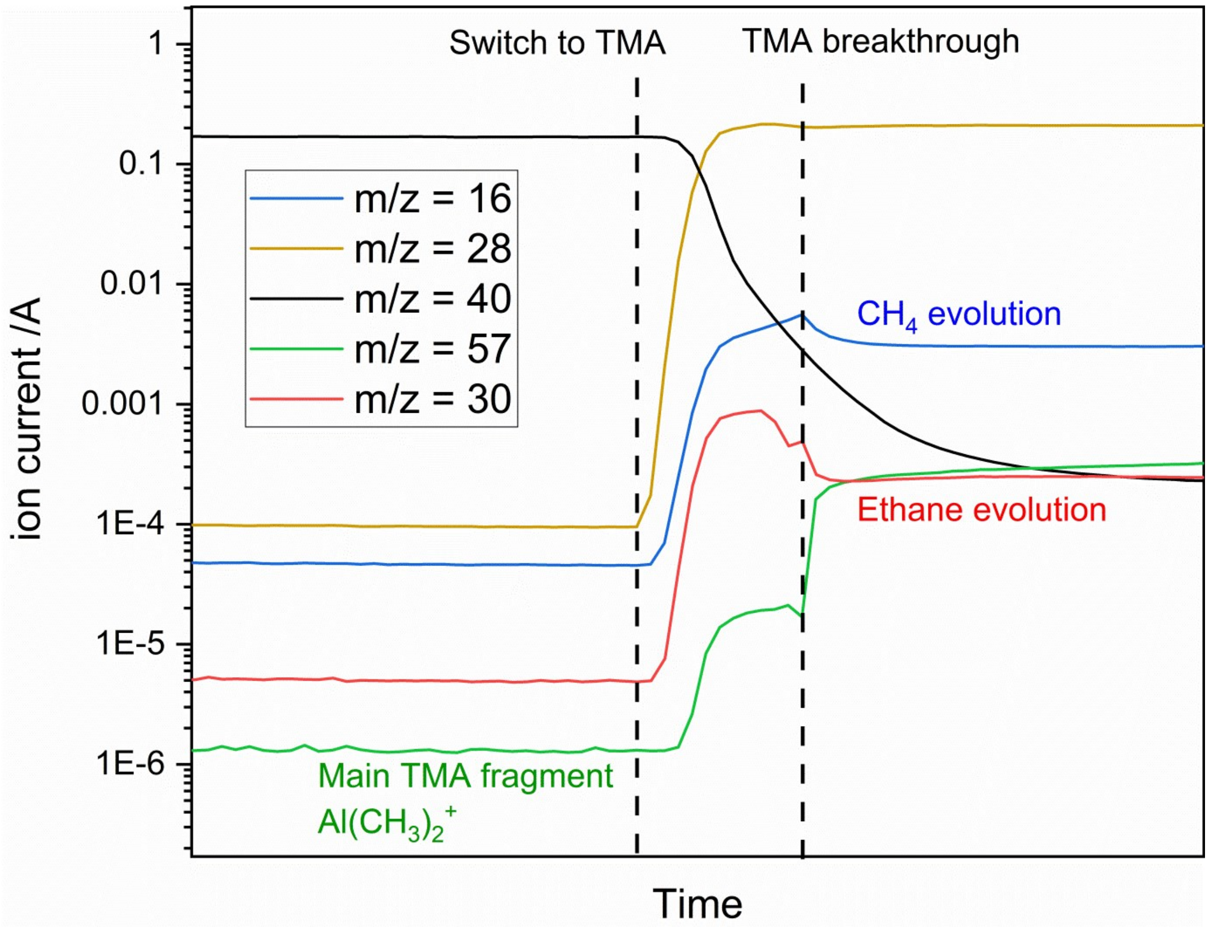

Fig. 11 Mass spectrometry during TMA dosing on V_2O_5 at 150 °C. Shown is the evolution of mass traces m/z = 57, m/z = 30 and m/z = 16 which are the strongest fragments for TMA, ethane and methane, respectively, during the reaction in the very first half cycle. Please note that the fragmentation patterns are more complicated than this simple

assignment. Ar (m/z = 40) was used for purging and N_2 (m/z = 28) was used as carrier gas for TMA.

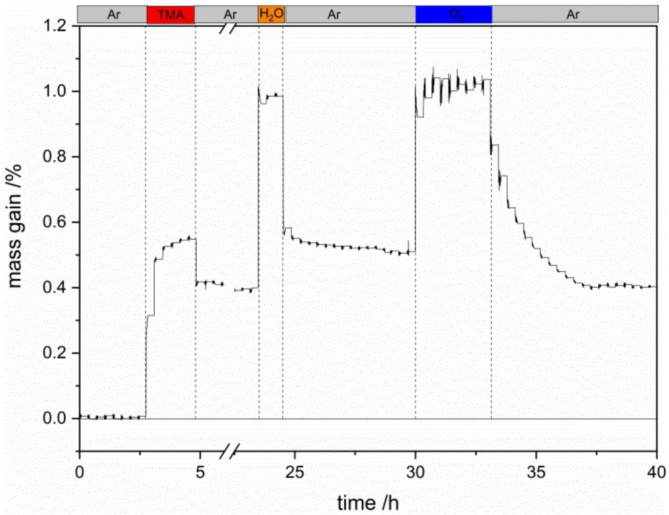

Fig. 12 Mass gain in magnetic suspension balance for reaction sequence TMA/H_2O/O_2 with TMA and water dosing at 50 °C and O_2 dosing at 450 °C.

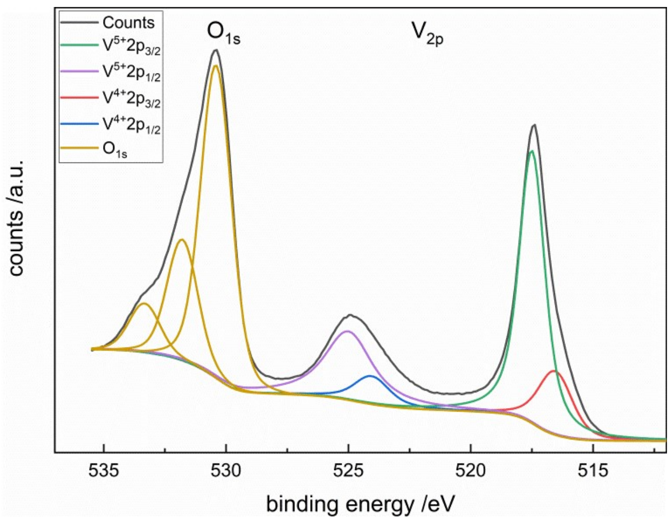

Fig. 13 XPS of PO_x/V_2O_5 after the first cycle of PO_x-ALD at 150 °C. Shown are the O_{1s} and V_{2p} spectra.

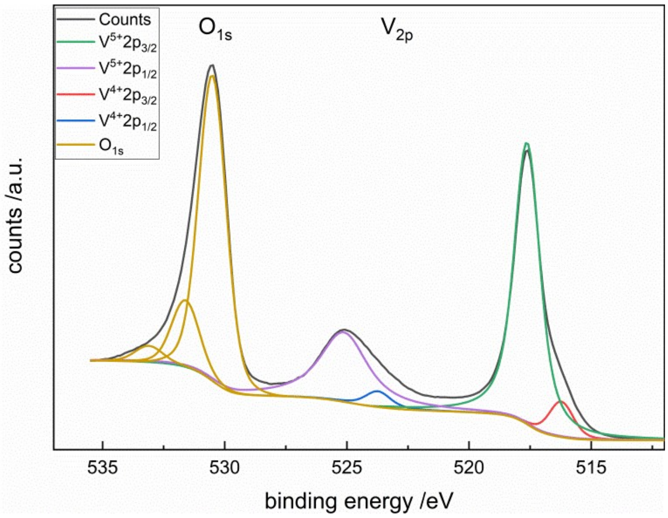

Fig. 14 XPS of PO_x/V_2O_5 after the first cycle of PO_x-ALD at 450 °C. Shown are the O_{1s} and V_{2p} spectra.

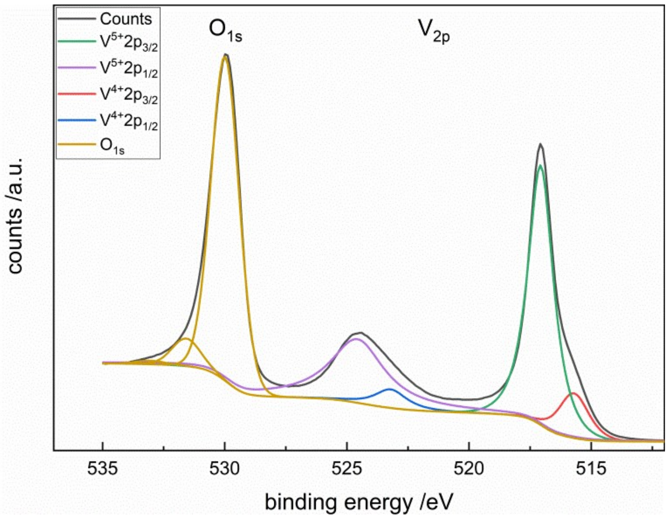

Fig. 15 XPS of V_2O_5 calcined at 450 °C. Shown are the O_{1s} and V_{2p} spectra.

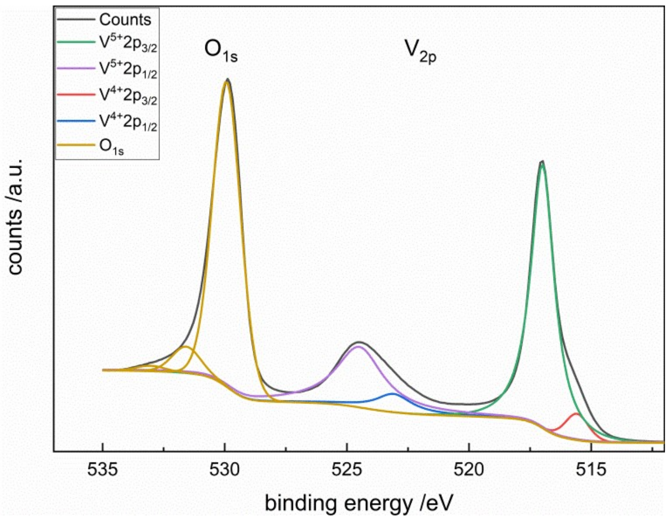

Fig. 16 XPS of fresh V_2O_5. Shown are the O_{1s} and V_{2p} spectra.

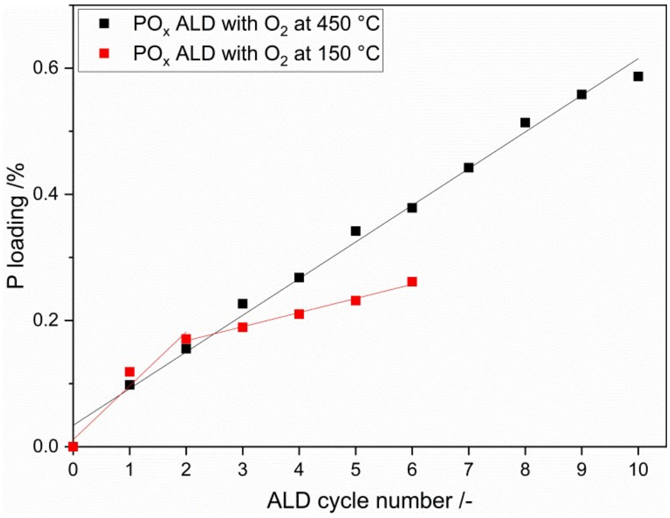

Fig. 17 Chemical analysis of P loading of ALD samples prepared at 450 °C by XRF (black) and ALD samples prepared at 150 °C by ICP-OES (red).

Table 1 Fit parameters for V2p$_{3/2}$ core level using Gaussian-Lorentzian functions for V^{5+} and V^{4+} fittings. Shown are the peak positions, full width at half maximum (FWHM), and the Lorentzian contribution. For deconvolution of the vanadium peak to V^{4+} and V^{5+} species, only the V2p$_{3/2}$ was used as the V2p$_{1/2}$ overlaps with an O1s satellite.

	V^{5+}2p$_{3/2}$		V^{4+}2p$_{3/2}$		
Sample	Peak BE (eV)	FWHM (eV)	Peak BE (eV)	FWHM (eV)	L/G Mix (%)
V_2O_5 fresh	517.08	1.26	515.68	1.49	70
V_2O_5 calcined (450 °C)	516.98	1.16	515.58	1.17	95
PO_x/V_2O_5 1 half cycle	517.18	1.63	516.28	1.73	50
PO_x/V_2O_5 1 cycle (150 °C)	517.48	1.26	516.58	1.65	50
PO_x/V_2O_5 1 cycle (450 °C)	517.58	1.26	516.18	1.17	50
AlO_x/V_2O_5 1 half cycle	516.88	1.91	515.58	1.59	80
AlO_x/V_2O_5 1 cycle (150 °C)	517.18	1.57	515.78	1.39	40
AlO_x/V_2O_5 1 cycle (450 °C)	517.28	1.41	515.78	1.11	45