

Supplementary Materials: Deactivation of a vanadium-based SCR-catalyst used in a biogas-powered Euro VI heavy-duty engine installation

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In this supplementary material several XPS core level spectra of different key elements present in the catalyst material are compiled. All spectra are normalized to the background on the low binding energy side of the photoelectron signal without any background subtraction. Figure S1 displays a region of survey spectra containing the P 2p and S 2p region, respectively. Any signal that may originate from the s 2p levels appears to be below the detection limit of the measurement. The P 2p signal is similar for all samples. Note that trace amounts of phosphorus may be present in the TiO₂ support material as well. Hence this result indicates that nearly no phosphorus is transported to the SCR catalyst section from upstream parts of the emission control system.

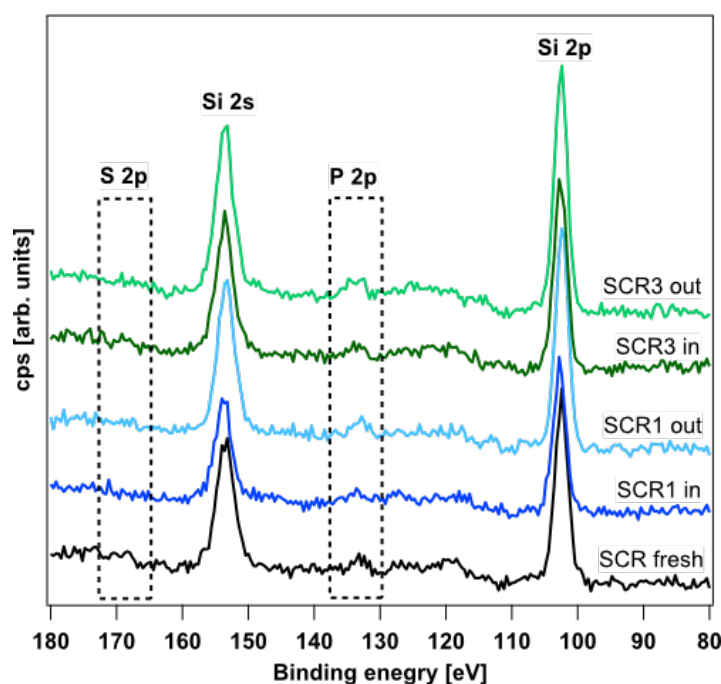


Figure S1. Fraction of survey spectra showing the S 2p and P 2p regions.

The O 1s spectra are depicted in Figure S2a). They consist of two distinct signals at about 530 eV and above 532 eV as discussed in the main text. Due to other oxides present in the samples, most prominently oxides of Ti, V, Si, W, a clear assignment is difficult. Additionally, final state satellites of the V 2p signal present in the O 1s region would further complicate a deconvolution of the signal [1]. While the signal at 530 eV is clearly connected to oxygen atoms in metal oxides the signal group at around 532 eV has several origins. Oxygen in SiO₂ is found at about 532 eV [2] while OH groups on metal oxides are as well found in the same binding energy region [3]. Taking a closer look at the Si 2p spectra in Figure S2b), it can be seen that the outlet samples contain a slightly larger amount of silicon. This can certainly account for parts of the increased signal at 532 eV observed in the O 1s spectra. However, note further that the oxide-related signal at 530 eV becomes less intense for the outlet samples, which is an indication that the signal is attenuated at species on the surface. We speculate that

these species are additional OH groups formed on the surface at some point during or after operation of the catalyst. It remains unclear on which oxide or by which mechanism these hydroxides form. Those additional OH groups could, however, be at the origin of the limited adsorption of ammonia observed in the TPD experiments.

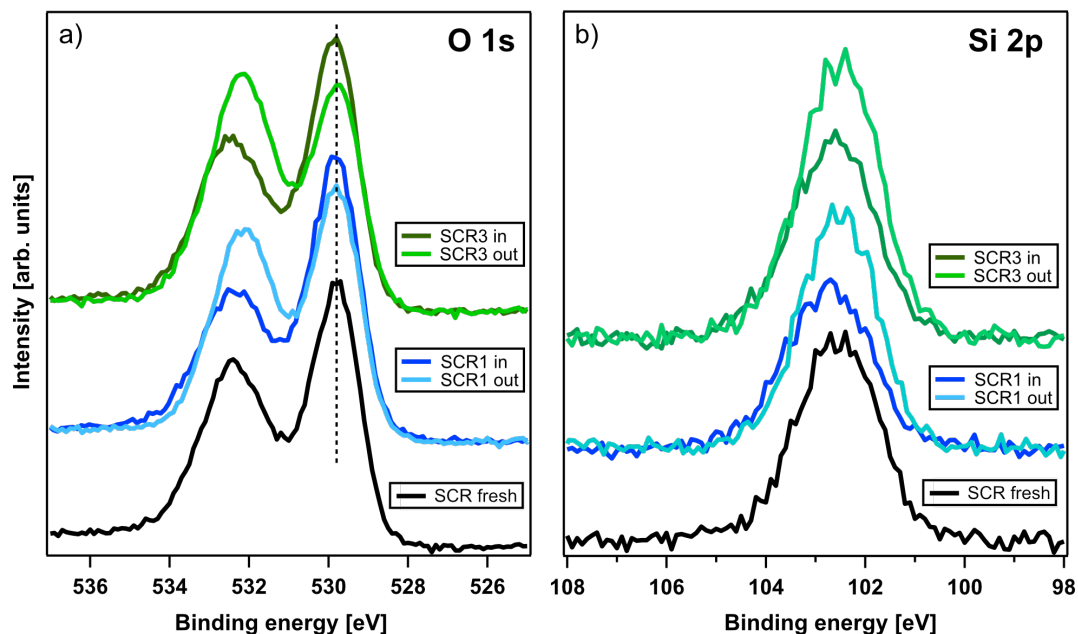


Figure S2. a) Oxygen 1s and b) silicon 2p spectra of the different SCR catalyst samples.

The titanium 2p signal in Figure S3a) exhibits slightly lower intensity for the outlet samples while the vanadium 2p signal in Figure S3b) shows a bit higher intensity. This is likely caused by slightly different washcoat thickness on the outlet part of the catalyst samples, resulting in a higher coverage of the TiO₂ support with the vanadium-containing wash coat. However, the total amount of oxide material at the surface accessible to the XPS measurement should be the same for the inlet and outlet samples, respectively. Hence the assumption on the OH groups made above based on the O 1s signals is expected to still be valid.

In Figure S4 tungsten 4f spectra are shown. They overlap with a broad vanadium 3p signal and thus the spectral shape appears unusual with an apparent higher intensity on the 4f_{5/2} side of the spectrum. However, no significant changes between the catalyst samples are observed. Only the SCR3 outlet sample appears to contain slightly less tungsten at the surface.

References

1. Silversmit, G.; Depla, D.; Poelman, H.; Marin, G.B.; De Gryse, R. Determination of the V2p XPS binding energies for different vanadium oxidation states (V5+ to V0+). *Journal of Electron Spectroscopy and Related Phenomena* **2004**, *135*, 167–175. doi:10.1016/j.elspec.2004.03.004.
2. Wu, J.X.; Wang, Z.M.; Ma, M.S.; Li, S. X-ray photoemission studies of praseodymium thin films on SiO₂/Si(100). *Journal of Physics-Condensed Matter* **2003**, *15*, 5857–5864. doi:10.1088/0953-8984/15/34/315.
3. Dupin, J.C.; Gonbeau, D.; Vinatier, P.; Levasseur, A. Systematic XPS studies of metal oxides, hydroxides and peroxides. *Physical Chemistry Chemical Physics* **2000**, *2*, 1319–1324. doi:10.1039/a908800h.

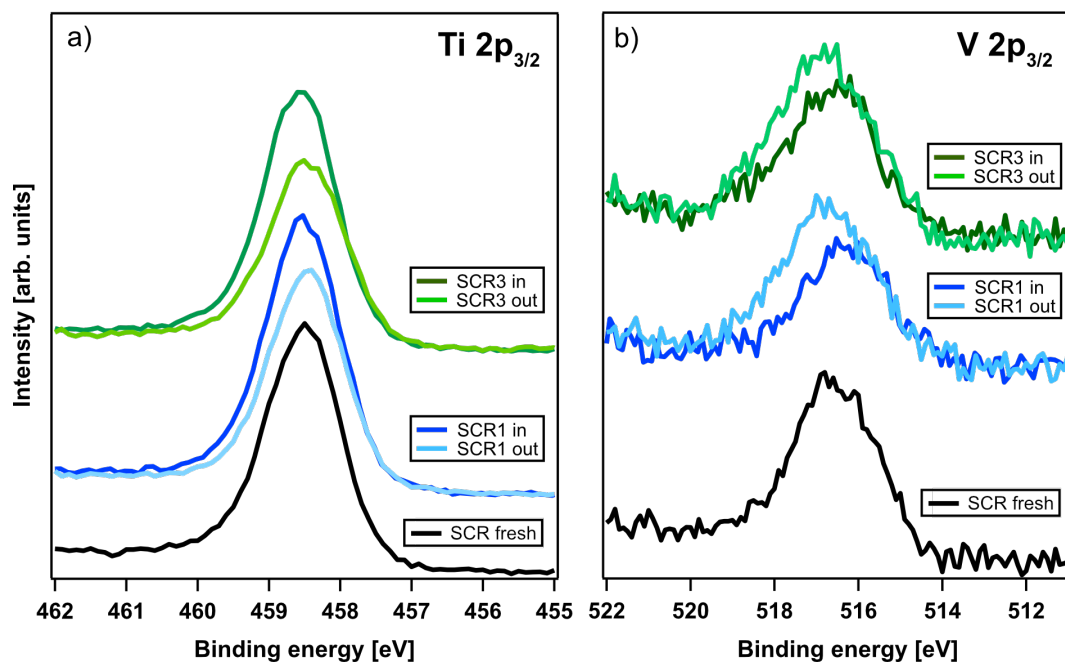


Figure S3. a) Titanium $2p_{3/2}$ and b) vanadium $2p_{3/2}$ spectra of the different catalyst samples.

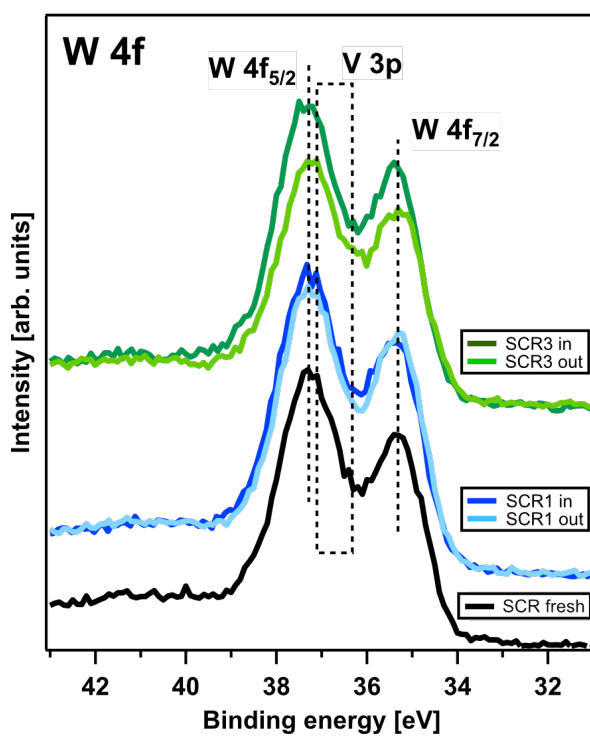


Figure S4. W $4f$ spectra of the different catalyst samples.