S1. Vibrational experiments on chemisorption on monolayer VS$_2$

To elucidate the eventual formation of surface vanadium-oxide phases, we have carried out a vibrational investigation by high-resolution electron energy loss spectroscopy (HREELS) on monolayer VSe$_2$ on graphite, which was prepared using the exact experimental procedures reported in the Experimental methods of the paper by Bonilla et al.\textsuperscript{1}.

The use of HREELS provides unambiguous fingerprint regarding surface chemical bonds and adsorption at solid surfaces. Specifically, the inspection of the HREELS spectrum is a particularly powerful tool to identify vanadium-oxide phases and, correspondingly, the oxidation status of V atoms. As a matter of fact, VO$_2$ is characterized by surface phonons at 55 and 95 meV\textsuperscript{2}; V$_2$O$_3$ by an intense feature at 68 meV\textsuperscript{3}; and V$_2$O$_5$ by several modes at 45, 74, 105, and 126 meV\textsuperscript{4}. However, the vibrational spectrum in Fig. R1 does not exhibit any feature even after exposure to $10^5$ L of O$_2$. This unambiguously excludes the formation of surface vanadium-oxide phases, that, if existing, do not cover more than 1-2\% of the surface area (corresponding to the minimal sensitivity of HREELS technique).

Notably, the vibrational spectrum remains featureless even after exposure to $10^5$ L of H$_2$, H$_2$O and CO. The absence of adsorbate-related vibrational modes proves the chemical inertness of monolayer VSe$_2$ to most common gases, thus experimentally validating our theoretical model concerning chemical reactivity.

We also recorded the vibrational spectrum for the surface kept one year in air. The spectrum is dominated by C-H bending and stretching vibrations at 171 and 365 meV\textsuperscript{5}, respectively. This could
arise from hydrocarbon contamination from ambient air adsorbed at Se vacancies of the VSe$_2$ monolayer.

Figure S1: Vibrational spectra for monolayer VSe$_2$ grown on highly oriented pyrolytic graphite (HOPG) and the same surface modified by the exposure of O$_2$, H$_2$, H$_2$O and CO. The vibrational spectrum for the same surface kept one year in air is also reported.

REFERENCES