



Supporting Information

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Adsorption and Decomposition of DMMP on Size-Selected $(\text{WO}_3)_3$ Clusters

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Experimental Section

$(\text{WO}_3)_3^-$ cluster anions were prepared by a magnetron sputtering source in a cluster deposition apparatus described elsewhere.^[1] The metal oxide clusters were produced by reactive sputtering of a tungsten metal target with a mixture of argon, helium and oxygen gas. The as-produced clusters were electrostatically extracted and then guided into a magnetic sector mass spectrometer (25° sector magnet with resolution of $m/\Delta m = 20$). By tuning the magnetic field strength, the $(\text{WO}_3)_3^-$ cluster anions were mass-selected and focused by ion optics before entering the deposition chamber, where they were decelerated and soft-landed ($<1\text{eV}$) onto a freshly peeled HOPG surface. The resulting sample can be cooled to approximately $-170\text{ }^\circ\text{C}$ by liquid nitrogen (LN_2) or heated via resistive heating by passing current through the HOPG, with the temperature of the sample being monitored by a K-type thermocouple spring loaded to the back of the HOPG. A TPR set-up, consisting of a Hiden HAL/3F PIC quadrupole mass spectrometer (QMS) mounted on a linear translator and covered with a glass shroud, was used to characterize the activity of the as-deposited clusters. In the TPR experiment, 1 Langmuir of DMMP was pre-dosed via a leak valve onto a freshly peeled HOPG surface cooled at $-173\text{ }^\circ\text{C}$ to form physisorbed layers of DMMP on the HOPG surface. After that, 6×10^{12} $(\text{WO}_3)_3$ oxide clusters were deposited into the physisorbed layers of DMMP. The number of clusters was calculated by the integrating the cluster current over the deposition time. This dosing sequence is used since the pre-formed DMMP matrix may help to stabilize the $(\text{WO}_3)_3$ clusters by minimizing the cluster-cluster interactions, i.e. sintering. After the cluster deposition, the surface temperature was first raised to $50\text{ }^\circ\text{C}$ to desorb the vast majority of physisorbed DMMP, and then ramped to $400\text{ }^\circ\text{C}$ with a ramping rate of $2\text{ }^\circ\text{C/s}$, while the desorbing species were monitored by QMS.

In addition, deposited samples could also be transferred *in vacuo* to an adjacent UHV chamber, where they were characterized by *in situ* XPS with non-monochromatic Mg K α -rays (1253.6 eV), with the ejected electron kinetic energy analyzed via a high energy hemispherical analyzer. In the XPS studies, a higher pressure of DMMP (5×10^{-7} torr) was dosed during the deposition at room temperature in order to saturate the adsorption sites on the clusters. Co-deposition of excess DMMP and the (WO₃)₃ clusters resulted in enough signal intensity for P(2p) regions. In both XPS and TPR studies, the DMMP was purified by several freeze-pump-thaw cycles before being background dosed through a UHV compatible leak valve.

Reference

- [1] a) X. Tang, D. Bumueller, A. Lim, J. Schneider, U. Heiz, G. Ganteför, D. H. Fairbrother, K. H. Bowen, *J. Phys. Chem. C* **2014**, *118*, 29278-29286; b) X. Tang, K. H. Bowen, F. Calvo, *Phys. Chem. Chem. Phys.* **2017**, *19*, 31168-31176; c) F. Calvo, K. Bowen, X. Tang, *J. Phys. Chem. C* **2014**, *118*, 1306-1317; d) X. Li, K. A. Wepasnick, X. Tang, Y. Wang, K. H. Bowen, D. H. Fairbrother, G. Gantefoer, *J. Vac. Sci. Technol., B* **2012**, *30*, 031806; e) B. Kiran, A. K. Kandalam, R. Rallabandi, P. Koirala, X. Li, X. Tang, Y. Wang, H. Fairbrother, G. Gantefoer, K. Bowen, *J. Chem. Phys.* **2012**, *136*, 024317.