Supporting Information

Degradation of Chemical Warfare Simulants over CeO_2 and Gd-doped CeO_2 Aerogels: Divergent Results of DMMP and DFP

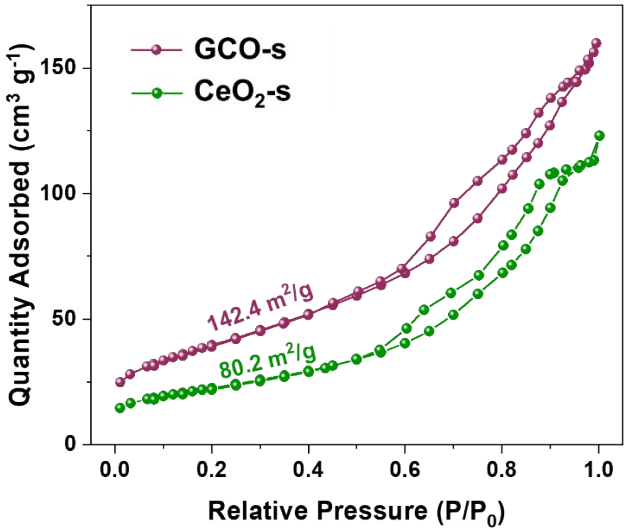

Figure S1. N_2 isotherms and calculated BET surface area of CeO_2 and GCO aerogels after the alkaline treatment.

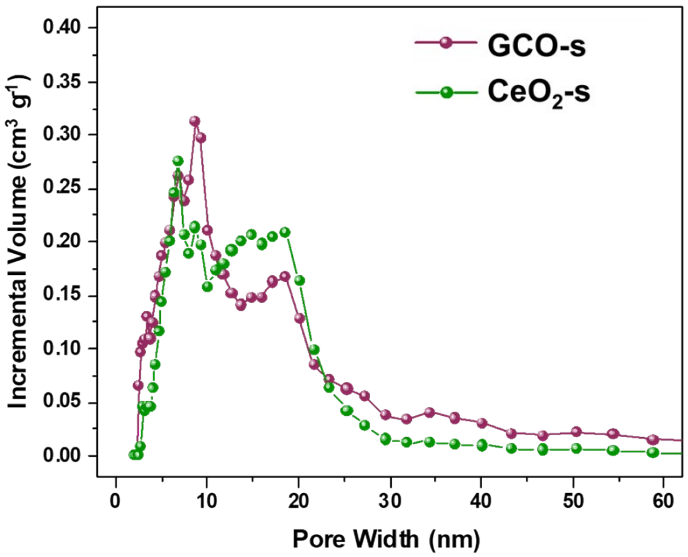

Figure S2. DFT pore size distribution of CeO_2-s and GCO-s aerogels.

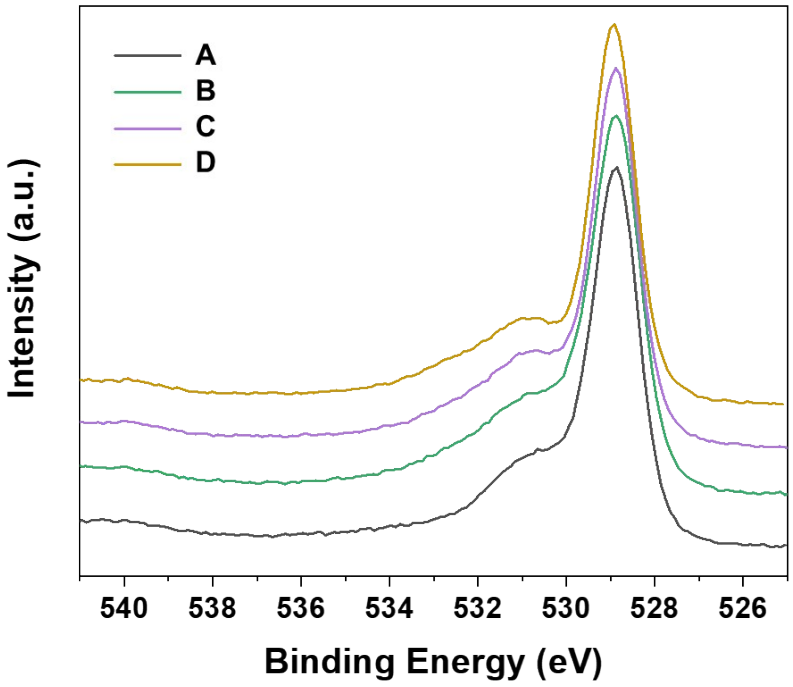

Figure S3. XPS O 1s analysis of commercial CeO_2 nanoparticles. A: pristine. B: alkaline treated. C: poisoned with HCl (pH = 5.0) then alkaline treated. D: poisoned with HCl (pH = 3.0) then alkaline treated.

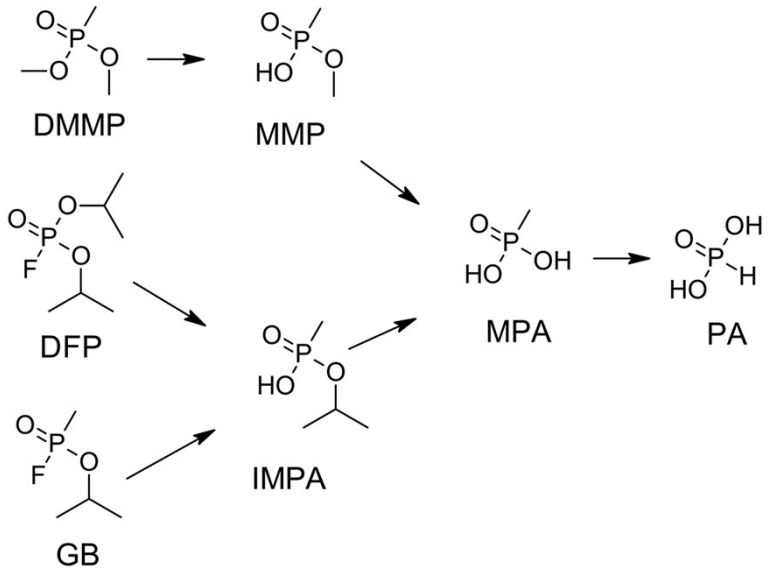

Figure S4. Potential pathway of DMMP, DFP, and GB degradation. MMP: methyl methylphosphonate. IMPA: isopropyl methylphosphonic acid. MPA: methylphosphonic acid. PA: phosphonic acid.

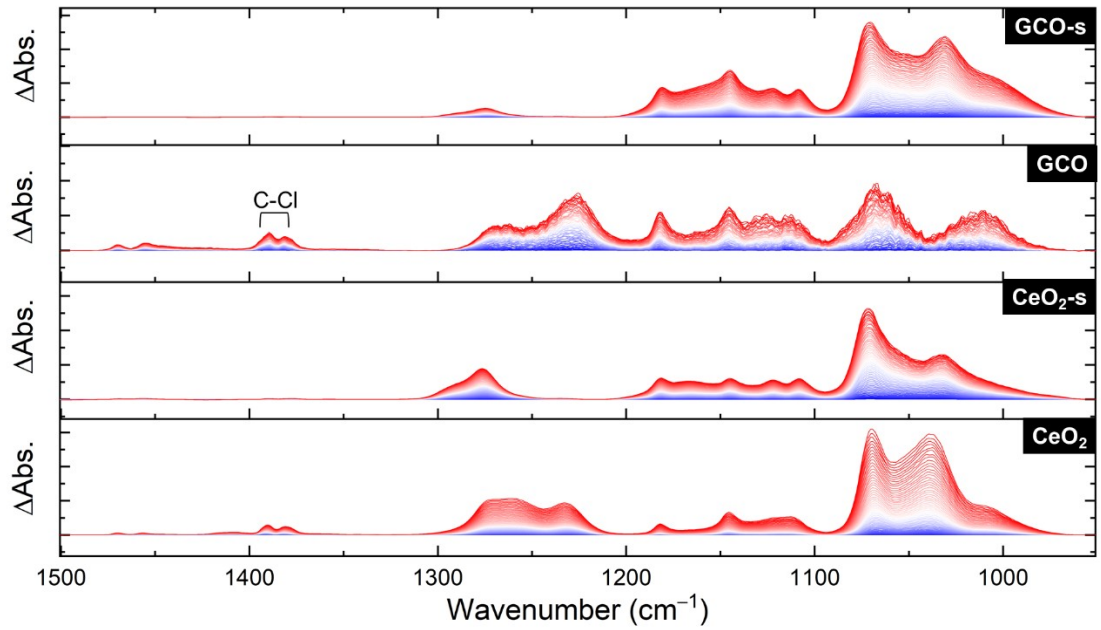

Figure S5. DRIFTS spectra under a N_2+O_2 purge recorded under broadband illumination. Spectra are recorded at 1 min intervals and progress from blue to red.

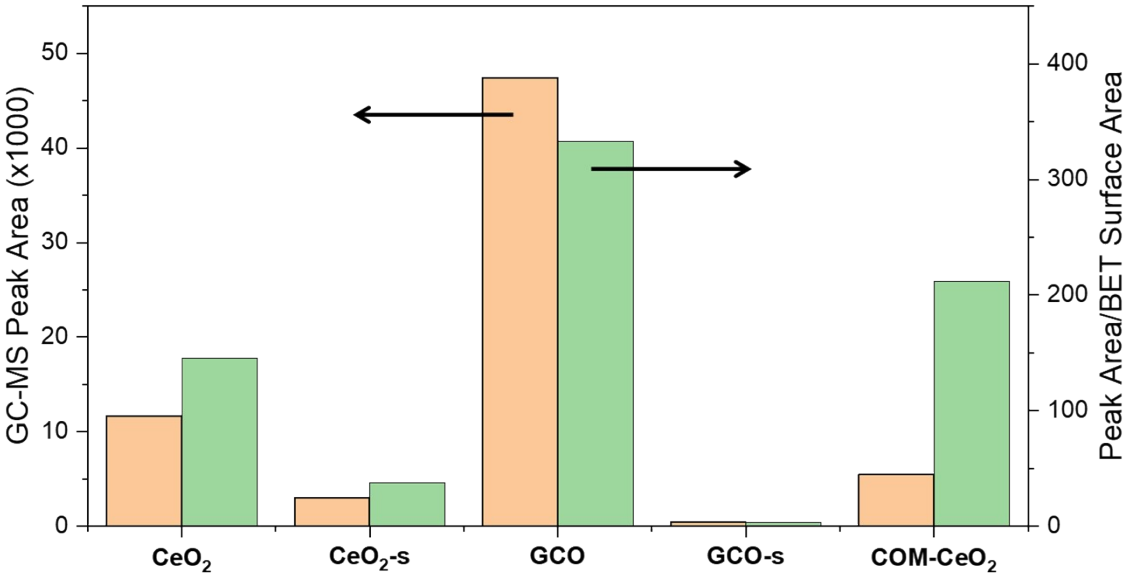

Figure S6. Intact DFP, as detected by dose-extraction GC-MS, over four aerogel variants and commercial CeO_2 powder (COM-CeO_2). Orange: raw values; green: values normalized to BET surface area of the respective material.

ATR-IR spectroscopy was performed in a custom UV reactor cell (Harrick Scientific Products, Inc.) in a Bruker VERTEX 70v FT-IR Spectrometer equipped with a tungsten global IR source and room-temperature DLaTGS detector. To prepare ATR samples, 30 mg of the aerogel powder was sonicated in 1.8 mL of DI water and then 500 µL was drop-cast onto a ZnSe internal reflection element (IRE) and dried overnight under flowing N_2. The IRE was sealed in the gas-tight cell and purged for 1 hour under 20% O_2 (N_2 balance) to remove water or loosely bound surface contaminants. The samples were dosed in a stream comprising 5 sccm of N_2 flowed through a DMMP bubbler balanced with 5 sccm O_2 and 15 sccm N_2. Scans were collected in 1 min intervals during 1 hour of dosing. After DMMP dosing, the ATR cell was purged with 5 sccm of O_2 and 20 sccm of N_2 with scans collected at 5 min intervals for 16 h.

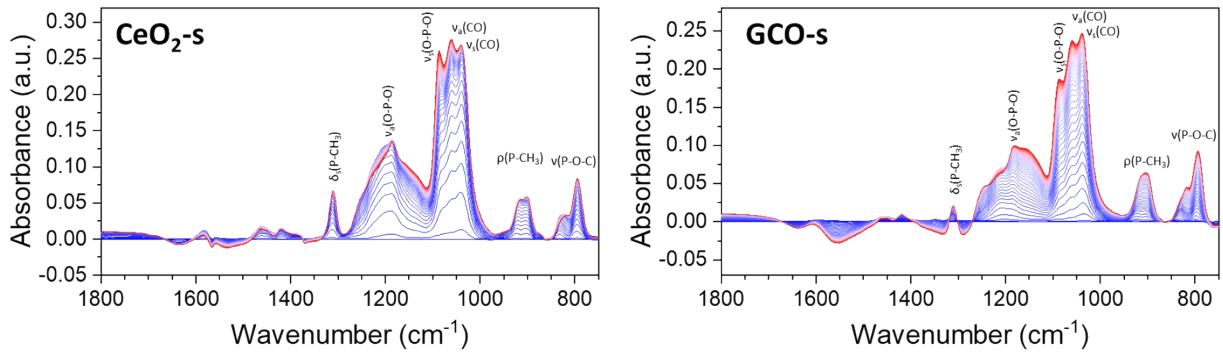

Figure S7. ATR spectroscopy during 1 hour of DMMP dosing on GCO-s and CeO_2-s aerogels. Scans are recorded at 1-minute intervals; colors progress from blue for first scan to red for final scan.

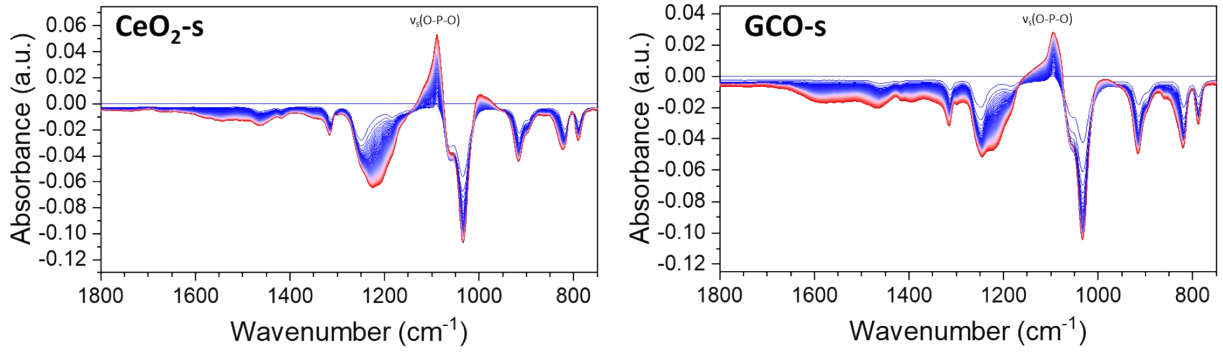

Figure S8. ATR spectroscopy during a 16-hour zero air purge after DMMP exposure. Scans are recorded at 5-minute intervals; colors progress from blue for first scan to red for final scan.

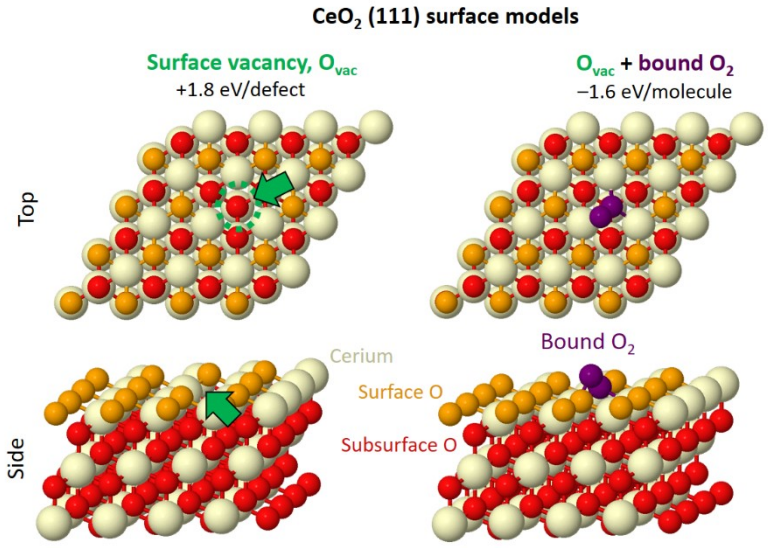

Figure S9. Atomic structures and energies calculated using DFT for the (111) CeO_2 surface with an oxygen vacancy (left) and with an O_2 molecule bound to an oxygen vacancy (right). The formation of an oxygen vacancy is thermodynamically unfavorable, but also significantly stabilizes bound O_2.

Table S1. Atomic partial charges for selected atoms in surface-adsorbate systems with oxygen vacancies and bound ROS.

Species	Atom	Charge (isolated)	Charge (bound)	Δ
Sarin	P	4.9079	4.9066	-0.0012
	F	-1.0256	-1.0196	0.0060
	O (P=O)	-1.8796	-1.8451	0.0345
	O (P-O-C)	-1.7186	-1.7027	0.0158
	C (P-C)	-1.2863	-1.3032	-0.0169
	Ce (P=O-Ce)	2.3991	2.4561	0.0570
	ROS O (top)	-0.5226	-0.5553	-0.0326
	ROS O (bottom)	-0.6724	-0.6680	0.0044
DIFP	P	4.9085	4.9067	-0.0018
	F	-1.0259	-1.0155	0.0104
	O (P=O)	-1.8701	-1.8500	0.0202
	O (O-C1)	-1.7143	-1.7071	0.0072
	O (O-C2)	-1.7234	-1.7165	0.0068
	Ce (P=O-Ce)	2.3991	2.4535	0.0544
	ROS O (top)	-0.5226	-0.5521	-0.0295
	ROS O (bottom)	-0.6724	-0.6638	0.0086
DMMP	P	4.9085	4.9049	-0.0035
	C	-1.2417	-1.2239	0.0178
	O (P=O)	-1.8565	-1.8340	0.0225
	O (O-C1)	-1.7381	-1.7306	0.0075
	O (O-C2)	-1.7479	-1.7306	0.0172
	Ce (P=O-Ce)	2.3991	2.4539	0.0548
	ROS O (top)	-0.5226	-0.5278	-0.0052
	ROS O (bottom)	-0.6724	-0.6614	0.0110

Table S2. Atomic partial charges for selected atoms in surface-adsorbate systems without oxygen vacancies and without bound ROS.

Species	Atom	Charge (isolated)	Charge (bound)	Δ
Sarin	P	4.9079	4.9065	-0.0014
	F	-1.0256	-1.0178	0.0078
	O (P=O)	-1.8796	-1.8571	0.0225
	O (P-O-C)	-1.7186	-1.7060	0.0125
	C (P-C)	-1.2863	-1.2884	-0.0022
	Ce (P=O-Ce)	2.3864	2.4537	0.0673
DIFP	P	4.9085	4.9074	-0.0011
	F	-1.0259	-1.0164	0.0095
	O (P=O)	-1.8701	-1.8496	0.0205
	O (O-C1)	-1.7143	-1.7007	0.0136
	O (O-C2)	-1.7234	-1.7129	0.0105
	Ce (P=O-Ce)	2.3864	2.4605	0.0740
DMMP	P	4.9085	4.9032	-0.0053
	C	-1.2417	-1.1878	0.0539
	O (P=O)	-1.8565	-1.8482	0.0083
	O (O-C1)	-1.7381	-1.7203	0.0179
	O (O-C2)	-1.7479	-1.7303	0.0176
	Ce (P=O-Ce)	2.3864	2.4662	0.0798

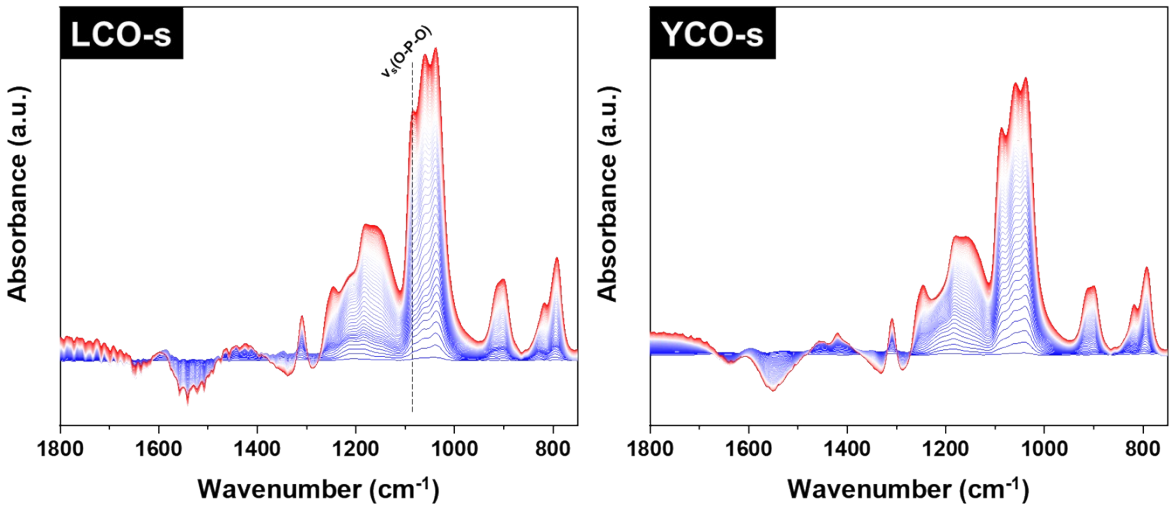

Figure S10. ATR spectroscopy during 1 hour of DMMP dosing on LCO-s and YCO-s aerogels. Scans are recorded at 1-minute intervals; colors progress from blue for first scan to red for final scan.