Electronic Supplementary Material

Probing the positions of TeO moieties in the channels of the MoVNbTeO M1 catalyst. A density functional theory model study

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Table of Contents

S1. Computational details

For the evaluation of the Coulomb and exchange integrals, we set the values of the parameters ITOL1, ITOL2, ITOL3, ITOL4, and ITOL5 done in CRYSTAL14 [1] to 7, 7, 7, 9 and 30, respectively. A SCF cycle was considered converged when the energy difference between successive iterations became lower than 10^{-7} a.u. A geometry optimization was assumed to be achieved when all of the following conditions were fulfilled: (*i*) the set of atomic displacements had a root mean square (RMS) value below 1.2×10^{-3} a.u. and the largest displacement was below 1.8×10^{-3} a.u; (*ii*) the RMS of the atomic energy gradients was below 3.0×10^{-4} a.u. with the largest value being lower than 4.5×10^{-4} a.u. In preparation for a full optimization with the program CRYSTAL14 and the B3LYP hybrid functional, we carried out a pre-optimization step with the program VASP [2-5] at the PBE+U level [6, 7] with U = 4 eV for Mo and V; the dispersion correction D2 [8] was added as well.

We do not expect a particular influence of the basis set superposition error in our systems because the neighboring situation of the TeO moiety is rather analogous in all positions probed.

S2. Tables

Table S1. Weighted average energies, $\varepsilon(n)$ (eV), of gap states of sites ***n***, reduced V centers or **2**(Mo), in a projected density of states. Distinct sites of the same type are distinguished by labels a–d, see Figure 1 of the main document.

Label	**1a**	**1b**	**2a**	**2b**	**3a**	**3b**	**3c**	**3d**	**7a**	**7b**	**7c**	**7d**
[7,7][7,7]	-1.53	-1.53			-1.39	-1.40	-1.39	-1.39	-1.71	-1.71	-1.70	-1.71
[7,2][7,2]	-1.79	-1.79			-1.77	-1.34	-1.77	-1.34	-2.06	-1.68	-2.06	-1.68
[2,7][7,2]	-1.70	-1.70			-1.61	-1.53	-1.53	-1.61	-1.75	-2.07	-2.07	-1.75
[2,7][3,2]	-1.76	-1.86			-1.93	-1.48	-1.67	-1.63	-1.93	-2.05	-1.85	-1.75
[2,3][3,2]	-2.02	-2.01			-2.10	-1.73	-1.72	-2.09	-2.11	-1.97	-1.96	-2.11
[2,2][2,2]			-1.88	-1.88	-1.76	-1.76	-1.76	-1.76	-1.90	-1.90	-1.90	-1.90

Table S2. Weighted average energies, $\varepsilon(n)$ (eV), of gap states of sites ***n***, in a projected density of states at various **2b**(Mo)–Te distances, *d*, during the linear scan of the Te position, Figure 4 of the main text.

	$\varepsilon(n)$			
d	**2b**	**3b**	**7d**	**8d**
322	-1.88	-1.76	-1.90	n/a
352	-1.51	-1.93	-1.78	n/a
383	-1.08	-2.08	-1.61	n/a
413	-0.75	-2.31	-1.42	n/a
443	-0.51	-2.37	-1.33	-0.44

S3. Figures

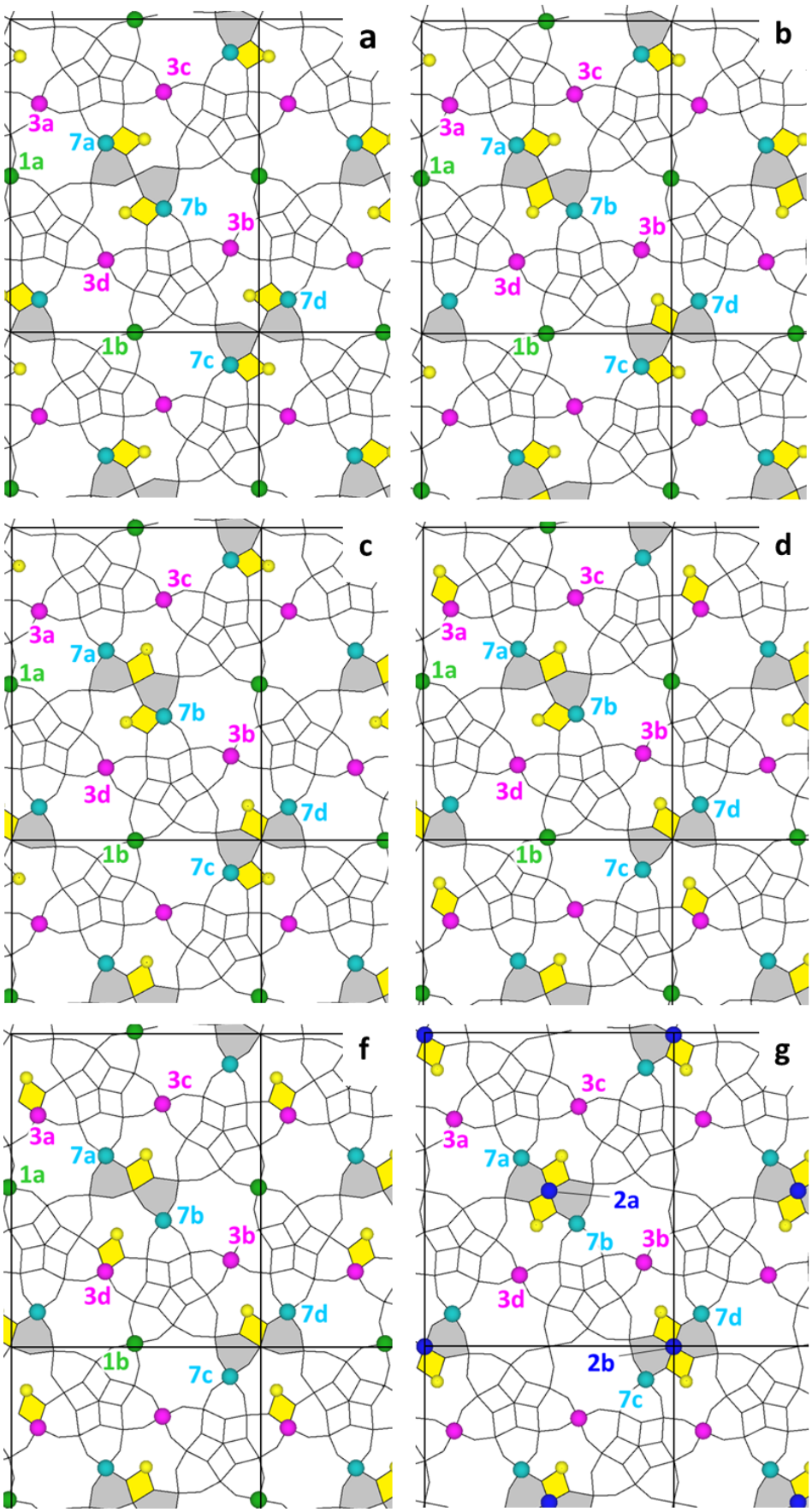

Figure S1. For the caption, see next page.

Figure S1 (see preceding page). [001] view of the framework in the M1 phase of MoVTeNbO with various locations of the TeO moieties in the hexagonal channels. The structures displayed in Table 1 of the main document with polaron distribution **1ab3abcd7abcd** in the configurations a) **[7,7][7,7]**, b) **[7,2][7,2]**, c) **[2,7][7,2]**, d) **[2,7][3,2]**, and e) **[2,3][3,2]**, as well as with polaron distribution **2ab3abcd7abcd** in the configuration g) **[2,2][2,2]**. V atoms occupy sites **1**, **3**, and **7**, see Figure 1 of the main document. Colored spheres indicate the location of the polarons. Gray areas denote the enclosed region between sites **2**(Mo), **4**(Mo), and **7**(V)**.** The limits of the unit cell are indicated by black lines.

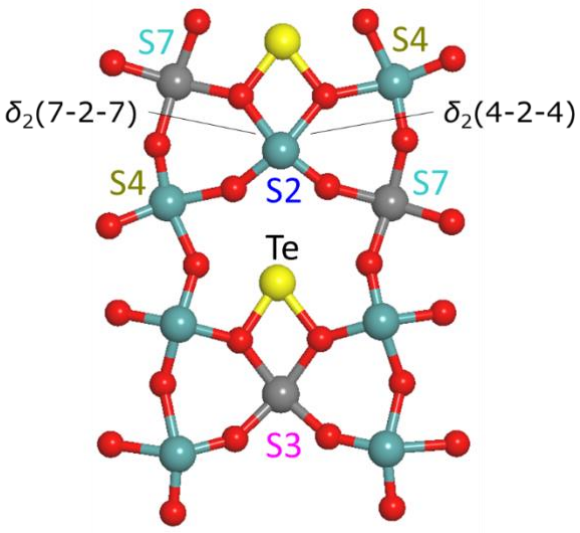

Figure S2. The hexagonal channel and its surrounding sites in the configuration **[3,2]** of the TeO moiety, i.e., one TeO moiety is next to center **3**(V), while the TeO moiety in the neighboring HC keeps a position close to **2**(Mo). The structural features δ_2 in both diagonals of the center **2**(Mo), **4**–**2**–**4** and **7**–**2**–**7**, range from 25 pm to 29 pm.

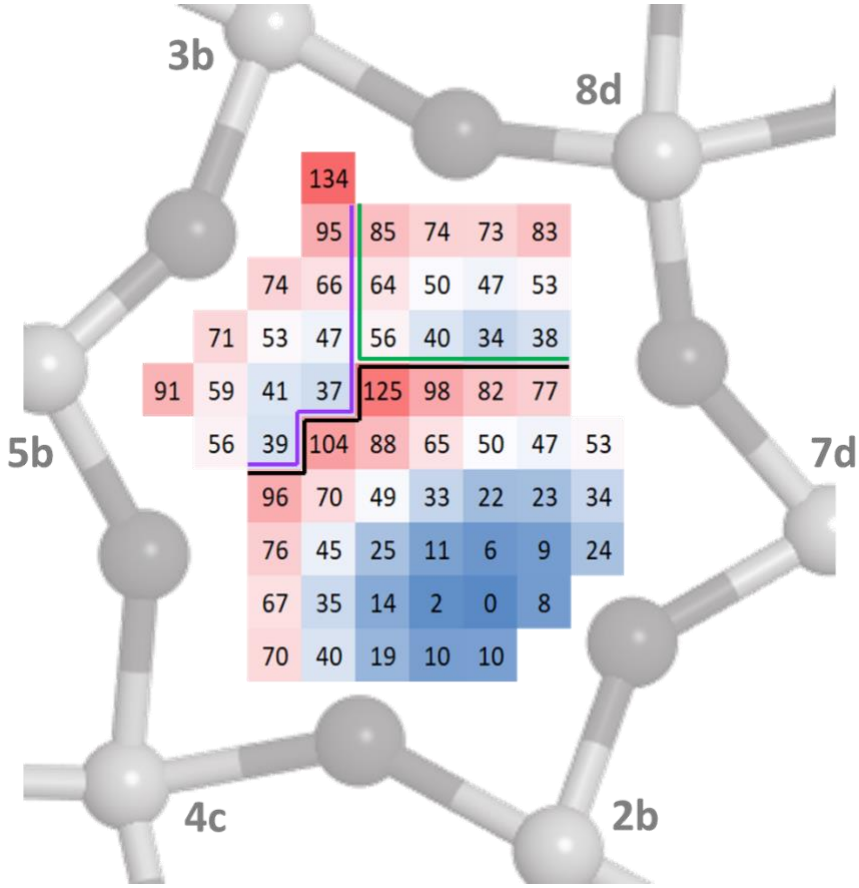

Figure S3. Relative energies, in kJ mol^{-1}, for the various scanned positions of the TeO moiety within the HC δ, according to the grid shown in Figure 3 of the main document. For the model chosen, the initial configuration, **[2,2][2,2]**, involves polarons at the centers **2b**(Mo), **3b**(V), and **7d**(V) of the sites forming the HC. For TeO locations outside the boundary indicated by a black line, the polaron at **2b**(Mo) relocates to either **5b**(Mo), indicated by the purple boundary, or **8d**(Mo), outlined by a green boundary; see also Figure 3 of the main document. The metal centers forming the HC are shown for reference only and are not to scale defined by the separation of the grid points.

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