Supporting information: Sodium promoter inducing a phase change in a palladium catalyst

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Supporting information.

In the Supporting Information, the cell parameters and atomic coordinates for the bulk phases considered in the paper are reported: cubic $NaPd_3O_4$, tetragonal $NaPd_3O_4$, $NaPd_3O_3$, and $NaPd_3O_6$. A diagram of the free energy of formation of the bulk phases calculated with LDA is reported. The projected density of states (PDOS) of the $NaPd_3O_4(100)$ surface with dissociatively adsorbed methane is shown. Finally, the electronic state localized on the O_{surf}-CH_3 bond is shown.

Table 1: Cell parameters (in Å) for the cubic $NaPd_3O_4$.

$\bar{a}_1$	5.80	0.00	0.00
$\bar{a}_2$	0.00	5.80	0.00
$\bar{a}_3$	0.00	0.00	5.80

Table 2: Atomic positions (in Å) for the cubic $NaPd_3O_4$.

Na	0.00	0.00	0.00	Na	2.90	2.90	2.90	Pd	1.45	2.90	0.00	Pd	4.35	2.90	0.00
Pd	2.90	0.00	1.45	Pd	2.90	0.00	4.35	Pd	0.00	1.45	2.90	Pd	0.00	4.35	2.90
O	1.45	1.45	1.45	O	4.35	1.45	1.45	O	1.45	4.35	1.45	O	4.35	4.35	1.45
O	1.45	1.45	4.35	O	4.35	1.45	4.35	O	1.45	4.35	4.35	O	4.35	4.35	4.35

Table 3: Cell parameters (in Å) for the tetragonal $NaPd_3O_4$.

$\bar{a}_1$	6.53	−0.01	0.00
$\bar{a}_2$	0.00	3.07	0.00
$\bar{a}_3$	0.00	0.00	5.57

Table 4: Atomic positions (in Å) for the tetragonal $NaPd_3O_4$.

Na	1.61	1.52	2.80	Pd	−0.26	0.00	0.01	Pd	3.47	−0.01	0.01	Pd	4.87	1.53	2.80
O	−0.16	1.53	1.38	O	−0.16	1.53	4.21	O	3.37	1.53	1.38	O	3.37	1.53	4.21

Table 5: Cell parameters (in Å) for $NaPd_3O_3$.

$\bar{a}_1$	11.53	−0.01	1.18
$\bar{a}_2$	0.00	3.04	0.00
$\bar{a}_3$	0.56	0.00	5.86

Table 6: Atomic positions (in Å) for $NaPd_3O_3$.

Na	0.57	0.00	2.32	Na	6.61	−0.01	2.41	Pd	−0.04	0.00	−0.52	Pd	3.93	0.00	1.21
Pd	7.75	−0.01	−0.29	Pd	3.00	1.51	4.92	Pd	9.26	1.51	2.87	O	−0.44	1.52	0.82
O	1.01	1.52	4.04	O	4.74	1.51	2.43	O	3.85	1.51	5.82	O	7.99	1.51	1.09
O	7.69	1.51	4.25												

Table 7: Cell parameters (in Å) for $NaPd_3O_6$.

$\bar{a}_1$	4.72	−2.73	0.02
$\bar{a}_2$	4.72	2.74	0.00
$\bar{a}_3$	0.00	−0.03	6.06

Table 8: Atomic positions (in Å) for $NaPd_3O_6$.

Na	4.78	−0.90	2.76	Pd	0.07	−0.03	−0.01	Pd	3.19	0.01	0.00	Pd	6.38	0.02	0.00
O	1.59	0.95	1.03	O	4.78	0.85	1.04	O	7.98	0.95	1.05	O	1.65	−0.92	−1.03
O	4.79	−0.91	−1.01	O	7.93	−0.91	−1.02								

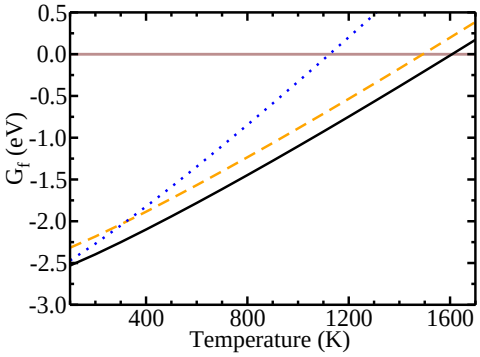

Figure 1: Free energies of formation of sodium-palladium oxides with respect to $NaPd_3$ and the oxygen gas at a pressure of 1 atm and temperatures between 100 K and 1700 K, calculated with LDA. Brown solid horizontal line: $NaPd_3$; black solid line: cubic $NaPd_3O_4$; orange dashed line: tetragonal $NaPd_3O_4$; blue dotted line: $NaPd_3O_6$.

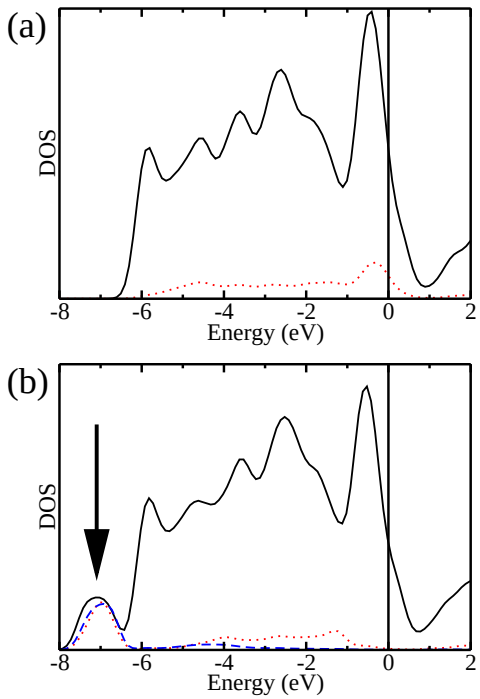

Figure 2: Density of states (DOS) of the $NaPd_3O_4(100)$ surface. (a) Clean surface; (b) surface with dissociatively adsorbed methane. Black line: total DOS; red dotted line: projected DOS (PDOS) on the 2p states of the surface oxygen forming the bond to the CH_3; blue dashed line: projected DOS on the 2p states of the C atom. The vertical black line corresponds to the Fermi energy. The PDOS of the 2p states have been multiplied by 3 to put them on the same scale as the total DOS. The large arrow indicates the new state appearing at the surface upon adsorption, mainly composed of 2p states of the surface oxygen and of the C atom, building a covalent bond. The electronic state corresponding to this peak is shown in Fig. 3S.

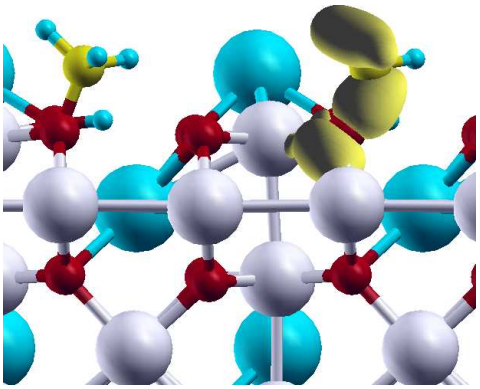

Figure 3: The electronic state relative to the peak shown by the arrow in Fig. 2S. Grey balls: palladium atoms; red balls: oxygen atoms; light blue atoms: sodium; yellow atoms: carbon; small light blue atoms: hydrogen. The yellow cloud is an isosurface of the surface state that is formed upon dissociative adsorption of methane. Both the spatial orientation and the PDOS of Fig. 2S suggest that this is mainly formed by the 2p states of oxygen and carbon.