Electronic Supplementary Information

Theoretical Insights into the Promotion Effect of Subsurface Boron for the Selective Hydrogenation of CO to Methanol over Pd Catalysts

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Table S1. Calculated activation energies (E_a) and reaction energies (ΔE) of the C-O bond dissociation of CHOH, CH_2O, CH_2OH and CH_3O on Pd(211) and Pd(211)-B, respectively, ZPE corrections are included.

	Pd(211)		Pd(211)-B	
	E_a(eV)	ΔE(eV)	E_a(eV)	ΔE(eV)
CHOH*+*→CH*+OH*	1.35	0.07	1.37	0.06
CH_2O*+*→CH_2*+O*	2.12	0.59	2.42	1.59
CH_2OH*+*→CH_2*+OH*	0.95	-0.14	1.03	0.33
CH_3O*+*→CH_3*+O*	1.55	0.28	1.78	1.19

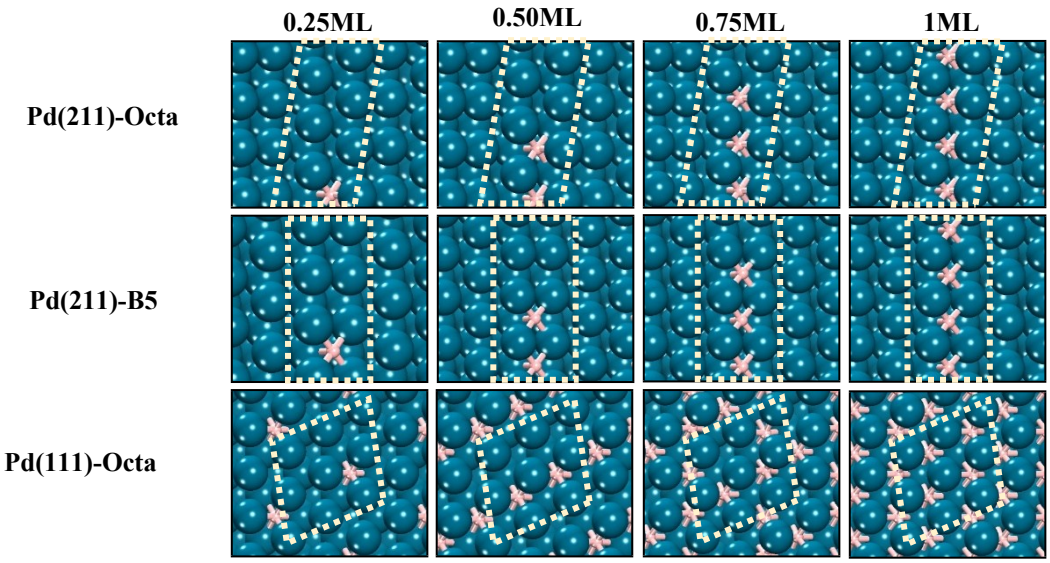


Figure S1. Illustration of the boron adsorption on Pd(211) at the octahedral site (Pd(211)-Octa) and B5 site (Pd(211)-B5) and Pd(111) at the octahedral site (Pd(111)-Octa) with the boron coverage of 0.25 ML, 0.50 ML, 0.75 ML and 1 ML, respectively.

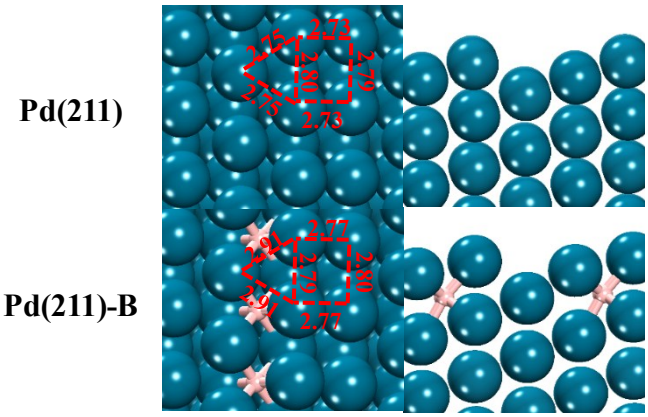
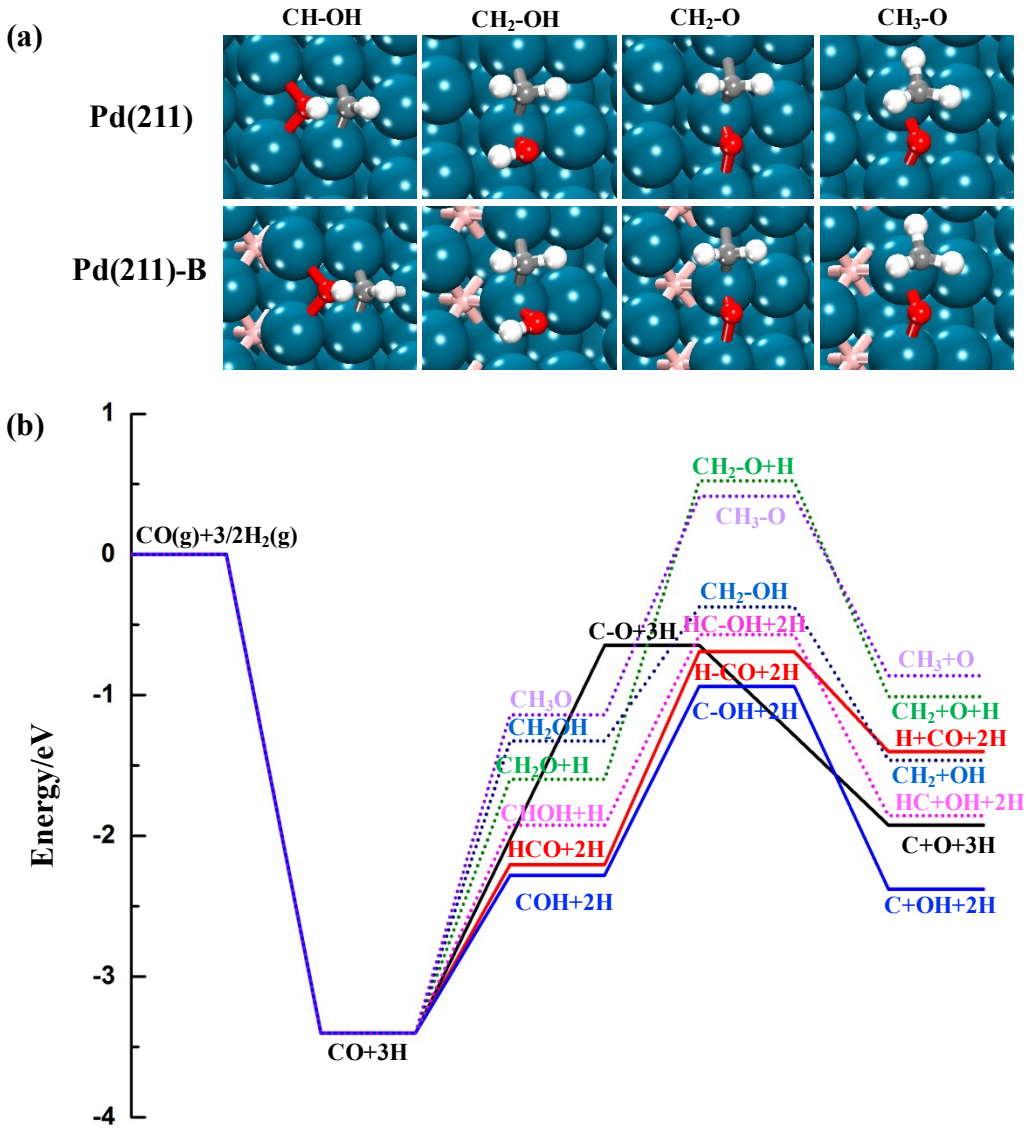


Figure S2. Top and side view of the structure of Pd(211) and Pd(211)-B used in this work, the red dash line and the corresponding number is the length of Pd-Pd bond on each surface (Å), which is marked to show the change of the bond length after the modification with boron atoms.


(a)
CH-OH
CH2-OH
CH2-O
CH3-O
Pd(211)
Pd(211)-B
(b)
Energy/eV
1
0
-1
-2
-3
-4
CO(g)+3/2H2(g)
CO+3H
CH2-O+H
CH3-O
CH2-OH
HC-OH+2H
C-O+3H
H-CO+2H
C-OH+2H
CH3O
CH2OH
CH2O+H
CHOH+H
HCO+2H
COH+2H
CH3+O
CH2+O+H
H+CO+2H
CH2+OH
HC+OH+2H
C+O+3H
C+OH+2H

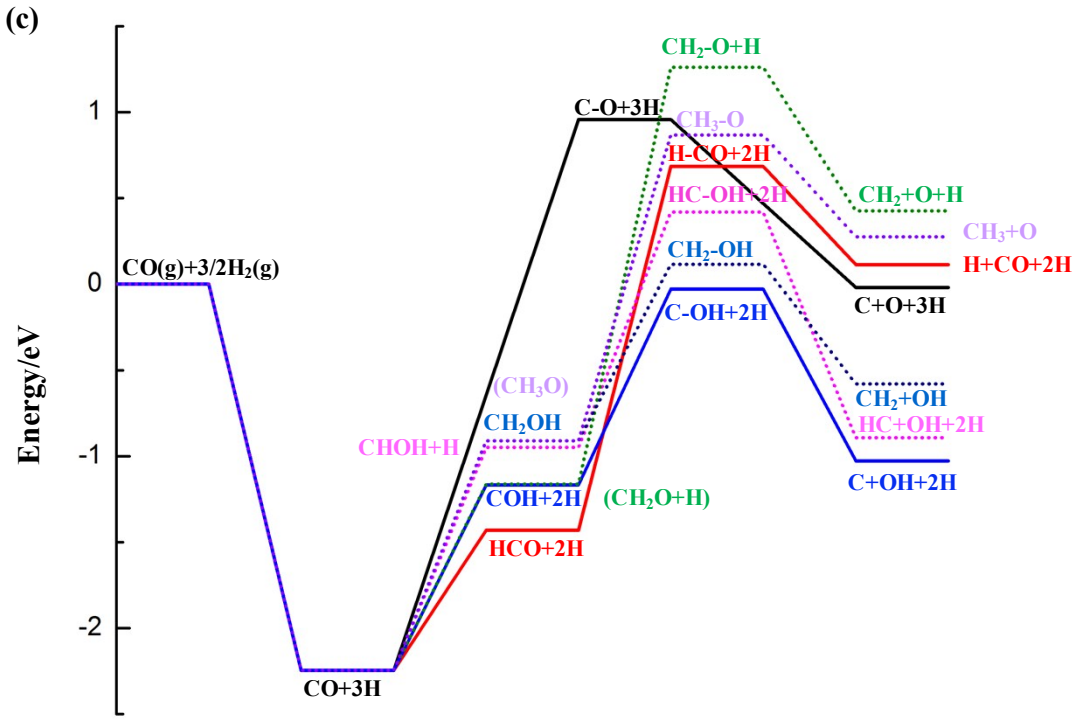


Figure S3. (a) Configurations of the transition states of elementary reactions shown in Table S1, (b) and (c) are the energy profiles of all possible C-O bond dissociation reactions considered on Pd(211) and Pd(211)-B, respectively.