

Electronic supplementary information

CO Tolerance of Pt₃Sn(111) Catalyst in Ethanol Decomposition

Xiaoqing Lu,^{a*} Zhigang Deng,^{a,b} Shuxian Wei,^a Qing Zhu,^a Weili Wang,^a Wenyue Guo^{a*} and Chi-Man Lawrence Wu^{b,c}

^a*College of Science, China University of Petroleum, Qingdao, Shandong 266580, P. R. China*

^b*Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, P. R. China*

^c*Key Laboratory for Applied Technology of Sophisticated Analytical Instruments, Shandong Academy of Sciences, Jinan, P. R. China*

*Corresponding authors: Xiaoqing Lu, Wenyue Guo

E-mail address: luxq@upc.edu.cn and wyguo@upc.edu.cn

Telephone: 86-532-8698-3372; Fax numbers: 86-532-8698-3363

1. Elementary reaction

Acetyl Oxidation. Under the oxidative conditions, CH₃CO can oxidize easily by OH group to form CH₃COOH. As shown on Figure S2 (f1), this process starts with the CH₃CO fragment and OH group locating at T^{Pt} site as the IS, ends with the CH₃COOH remaining at T^{Pt} site as the FS. In the TS, the OH group are close to the CH₃CO fragment, and the O atom of OH group and the C atom of CH₃CO form a newly C^α-O bond with the length of 1.81 Å. The energy barrier of this reaction is only 0.38 eV and the reaction energy is exothermic by 1.09 eV.

H + H → H₂. As shown in the Figure S2, the two H atoms are adsorbed at adjacent H^{3Pt} and F^{3Pt} sites as the IS. The diffusions of both H atoms form the TS, in which the two H atoms bind at top site with H-H distance of 1.144 Å. After the TS, the two H atoms approach each other forming FS. This process has an energy barrier of 0.71 eV, and is endothermic by 0.75 eV. For the newly-formed H₂ molecule, it is easy to escape from the Pt₃Sn(111) surface due to the weak adsorption energy about 0.1 eV at different adsorption sites.

2. Microkinetic model

We applied the microkinetic modeling technique to examine the oxidation of ethanol on Pt₃Sn(111). All of steps included in the microkinetic model are summarized in Table 4 (see the main manuscripts). Step 1 were assumed to be in equilibrium and the equilibrium constant K was estimated according to $K = \exp[-(\Delta E_{ads} - T\Delta S)/k_B T]$, in which ΔE_{ads} is the binding energy of CH₃CH₂OH on Pt₃Sn(111), while ΔS is the entropy change of the corresponding adsorbate induced by adsorption. The other steps were described by the forward rate.

The site balance of intermediate species included in the reaction can be written in terms of coverage (θ_X ; X = surface species):

$$\theta_{CH_3CH_2OH} + \theta_{CH_3CH_2O} + \theta_{CH_3CHO} + \theta_{CH_3CO} + \theta_{CH_2CO} + \theta_{CO} + \theta_{CH_2} + \theta_{CH_3} + \theta_{CH_4} + \theta_H + \theta_{H_2} + \theta_* = 1 \quad (1)$$

The coverage of CH_3CH_2OH is $\theta_{CH_3CH_2OH} = p_{CH_3CH_2OH} K_1 \theta_*$, respectively. Other surface species including CH_3CH_2O , CH_3CHO , CH_3CO , CH_2CO , CO , CH_2 , CH_3 , CH_4 and H can be described according to the steady-state approximation as summarized below, where the production and consumption rates of each species are assumed to be equal:

$$1. \frac{d\theta_{CH_3CH_2O}}{dt} = r_2 - r_3 = k_2 \theta_{CH_3CH_2OH} \theta_* - k_3 \theta_{CH_3CH_2O} \theta_* = 0$$

$$\theta_{CH_3CH_2O} = \frac{k_2}{k_3} p_{CH_3CH_2OH} K_1 \theta_* \quad (2)$$

$$2. \frac{d\theta_{CH_3CHO}}{dt} = r_3 - r_4 = k_3 \theta_{CH_3CH_2O} \theta_* - k_4 \theta_{CH_3CHO} \theta_* = 0$$

$$\theta_{CH_3CHO} = \frac{k_2}{k_4} p_{CH_3CH_2OH} K_1 \theta_* \quad (3)$$

$$3. \frac{d\theta_{CH_3CO}}{dt} = r_4 - r_5 = k_4 \theta_{CH_3CHO} \theta_* - k_5 \theta_{CH_3CO} \theta_* = 0$$

$$\theta_{CH_3CO} = \frac{k_2}{k_5} p_{CH_3CH_2OH} K_1 \theta_* \quad (4)$$

$$4. \frac{d\theta_{CH_2CO}}{dt} = r_5 - r_6 = k_5 \theta_{CH_3CO} \theta_* - k_6 \theta_{CH_2CO} \theta_* = 0$$

$$\theta_{CH_2CO} = \frac{k_2}{k_6} p_{CH_3CH_2OH} K_1 \theta_* \quad (5)$$

$$5. \frac{d\theta_{CO}}{dt} = r_6 - r_{10} = k_6 \theta_{CH_2CO} \theta_* - k_{10} \theta_{CO} = 0$$

$$\theta_{CO} = \frac{k_2}{k_{10}} p_{CH_3CH_2OH} K_1 \theta_*^2 \quad (6)$$

$$6. \frac{d\theta_{CH_2}}{dt} = r_6 - r_7 = k_6 \theta_{CH_2CO} \theta_* - k_7 \theta_{CH_2} \theta_H = 0$$

$$\theta_{CH_2} = \frac{k_2 \theta_*}{k_7 \theta_H} p_{CH_3CH_2OH} K_1 \theta_* \quad (7)$$

$$7. \frac{d\theta_{CH_3}}{dt} = r_7 - r_8 = k_7 \theta_{CH_2} \theta_H - k_8 \theta_{CH_3} \theta_H = 0$$

$$\theta_{CH_3} = \frac{k_2 \theta_*}{k_8 \theta_H} p_{CH_3CH_2OH} K_1 \theta_* \quad (8)$$

$$8. \frac{d\theta_H}{dt} = r_2 + r_3 + r_4 + r_5 - r_7 - r_8 - 2r_9$$

$$= k_2 \theta_{CH_3CH_2OH} \theta_* + k_3 \theta_{CH_3CH_2O} \theta_* + k_4 \theta_{CH_3CHO} \theta_* + k_5 \theta_{CH_3CO} \theta_* - k_7 \theta_{CH_2} \theta_H - k_8 \theta_{CH_3} \theta_H - 2k_9 \theta_H^2 = 0$$

$$\theta_H = \sqrt{\frac{k_2 p_{CH_3CH_2OH} K_1}{k_9}} \theta_* \quad (9)$$

$$9. \frac{d\theta_{CH_4}}{dt} = r_8 - r_{11} = k_8 \theta_{CH_3} \theta_H - k_{11} \theta_{CH_4} = 0$$

$$\theta_{CH_4} = \frac{k_2}{k_{11}} p_{CH_3CH_2OH} K_1 \theta_* \theta_H \quad (10)$$

$$10. \frac{d\theta_{H_2}}{dt} = r_9 - r_{12} = k_9 \theta_H^2 - k_{12} \theta_{H_2} = 0$$

$$\theta_{H_2} = \frac{k_2}{k_{12}} p_{CH_3CH_2OH} K_1 \theta_*^2 \quad (11)$$

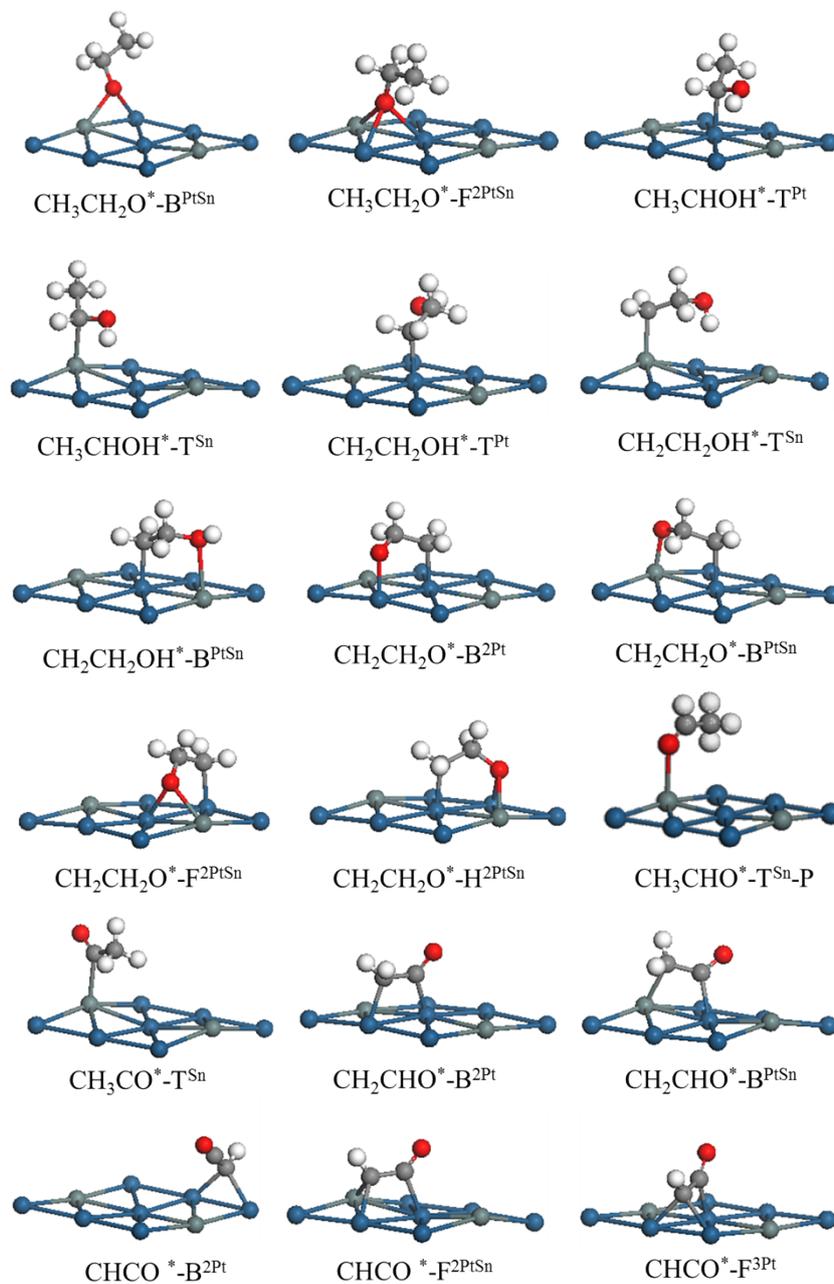
By putting all the coverage expressions into eq. 1, we can calculate θ_* and other surface coverages.

To test the effect of different partial pressure on the coverages, the calculations of the microkinetic model at 1, 2 and 3 atm are carried out in the range of 100 to 300 K, as shown in Table S1. These results show that with the pressure increases, the number of vacant sites θ_* decreases at the same temperature above 200 K; the coverage of CH_2CO increase at the same temperature from 100 to 300 K; and the θ_{CH_2} can reach the higher peak at higher ethanol partial pressure. These results indicate that the small increasing pressure has a minor effect on the coverages in the range of 100 to 300 K.

Table S1. Effect of temperature and ethanol partial pressure on the coverages of CH₂CO ($\theta_{\text{CH}_2\text{CO}}$), CH₂ (θ_{CH_2}) as well as vacant site (θ^*).

T (K)	1 atm			2 atm			3 atm		
	θ^*	$\theta_{\text{CH}_2\text{CO}}$	θ_{CH_2}	θ^*	$\theta_{\text{CH}_2\text{CO}}$	θ_{CH_2}	θ^*	$\theta_{\text{CH}_2\text{CO}}$	θ_{CH_2}
100	0.000	1.000	0.000	0.000	1.000	0.000	0.000	1.000	0.000
150	0.000	0.724	0.273	0.000	0.787	0.210	0.000	0.819	0.179
200	0.433	0.070	0.495	0.339	0.110	0.549	0.287	0.140	0.570
250	0.958	0.001	0.041	0.941	0.002	0.057	0.928	0.003	0.069
300	0.995	0.000	0.005	0.993	0.000	0.007	0.992	0.000	0.008

Figure S1. Configurations of reaction intermediates along reaction pathway of ethanol decomposition to CO on Pt₃Sn(111).



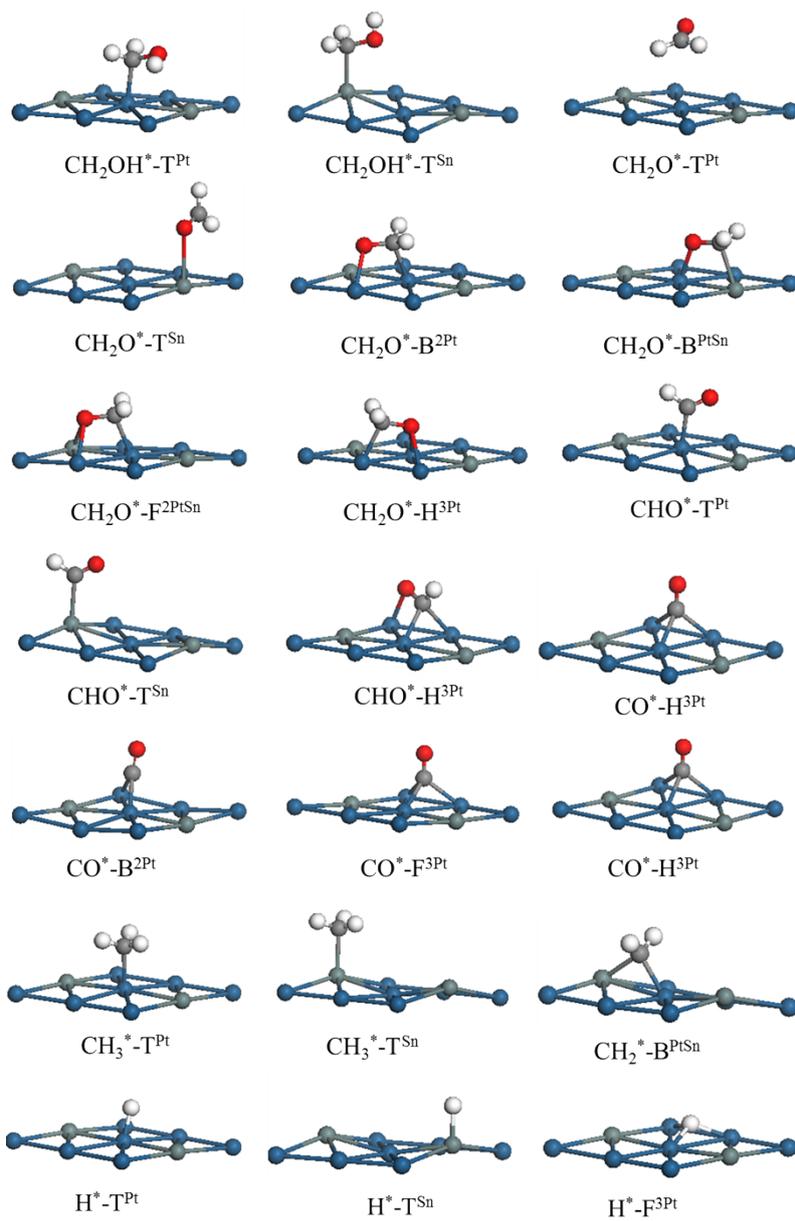
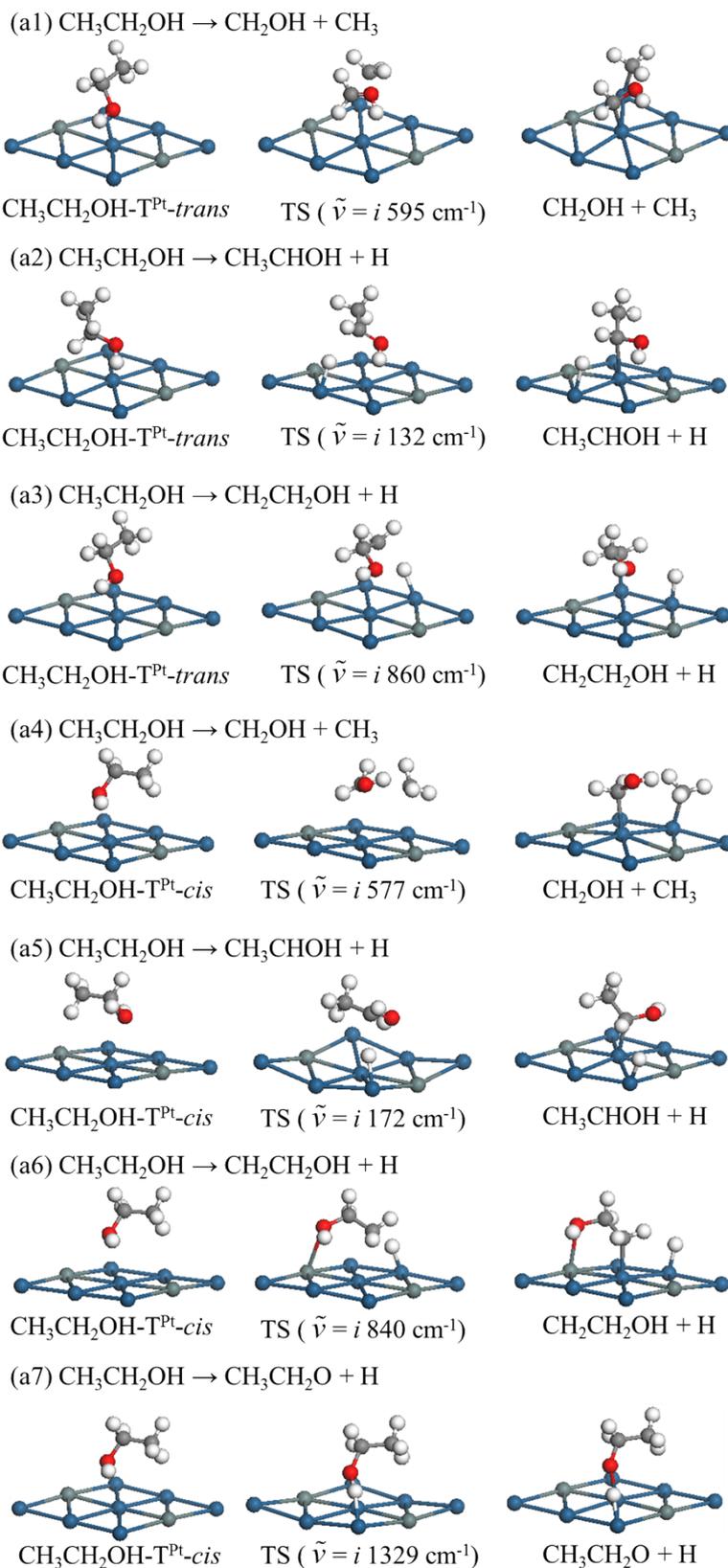
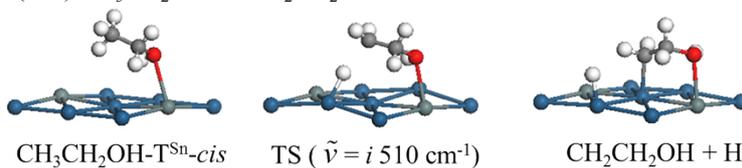
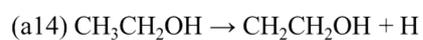
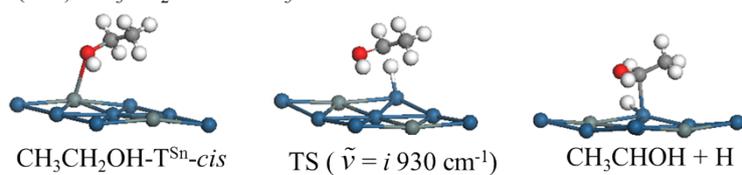
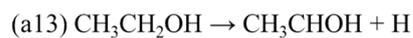
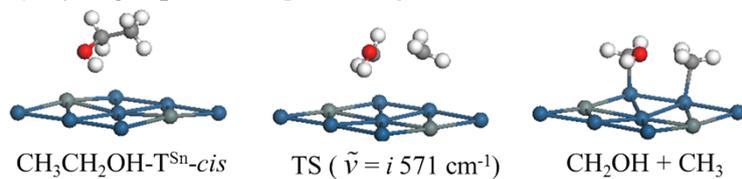
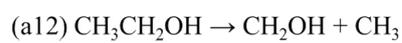
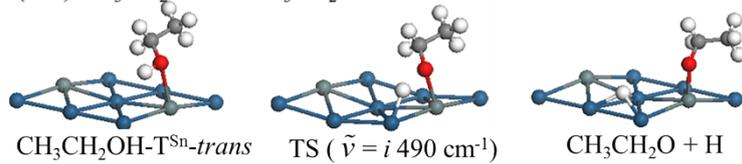
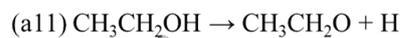
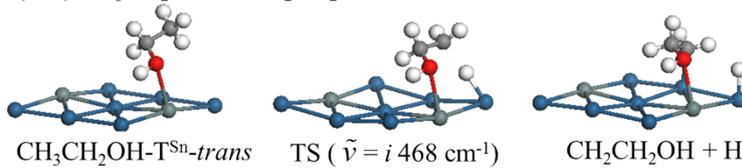
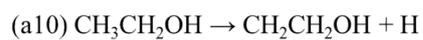
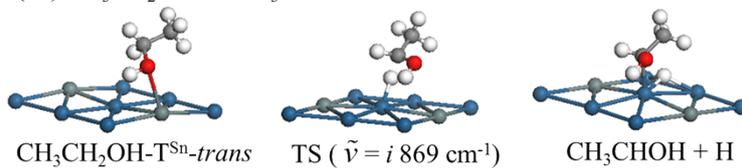
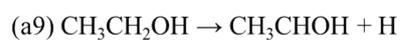
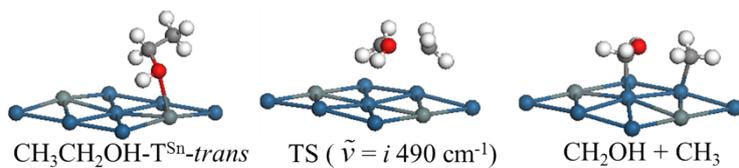
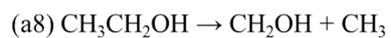
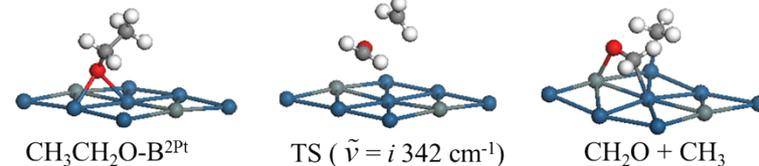
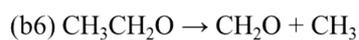
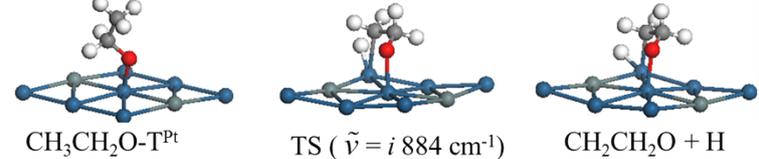
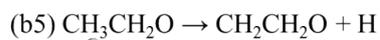
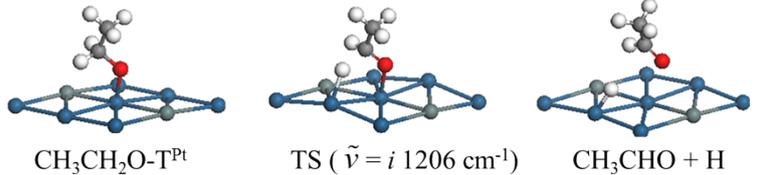
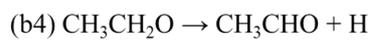
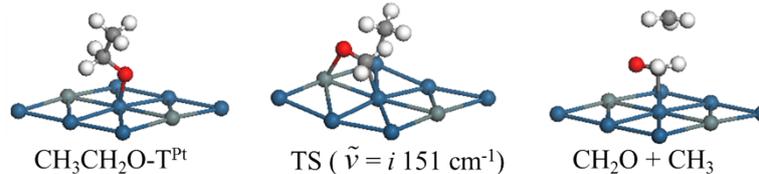
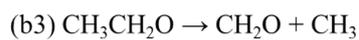
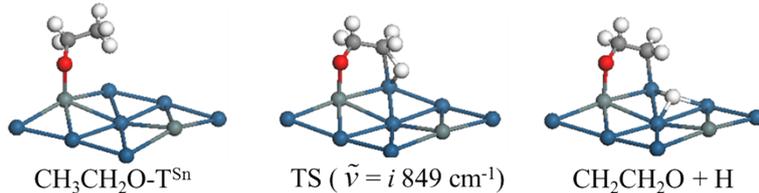
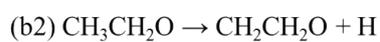
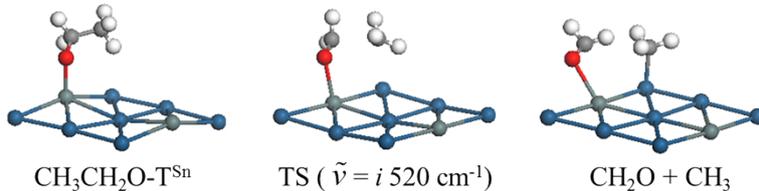
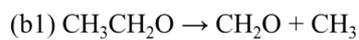
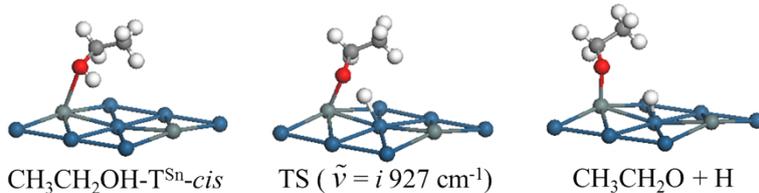
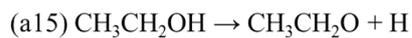


Figure S2. Calculated structures of the initial state, transition state, and final state involved in ethanol decomposition routes on Pt₃Sn(111).







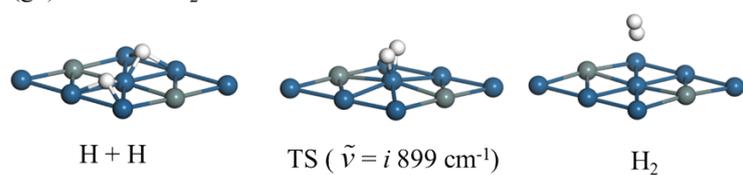
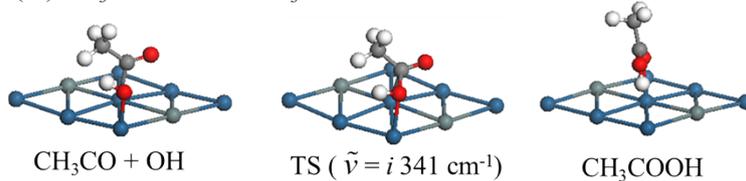
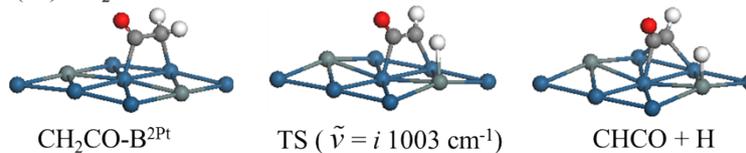
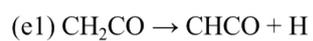
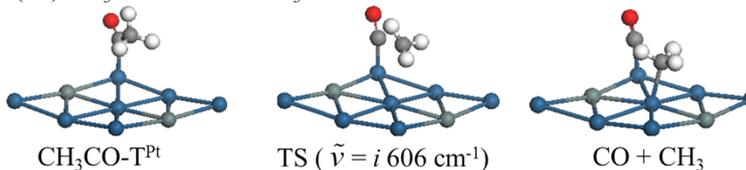
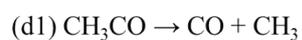
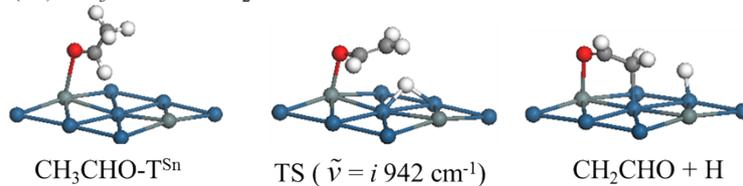
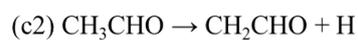
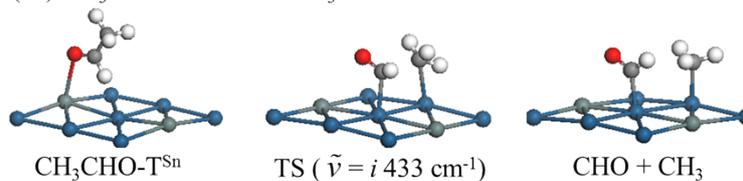
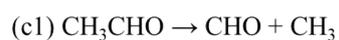
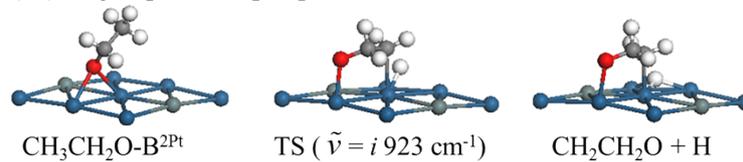
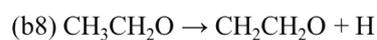
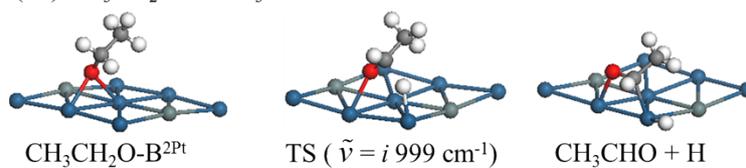
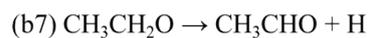


Figure S3. Calculated structures of the initial state, transition state, and final state involved in the CH_2CO decomposition on $\text{Pt}_3\text{Sn}(111)$ with a large (4×4) cell.

