

Supporting information

Electrocatalysis of Ethanol on Pd Electrode in Alkaline Media: an *in situ* ATR-SEIRAS Study

Yao-Yue Yang,^a Jie Ren,^b Qiao-Xia Li,^c Zhi-You Zhou,^{* b} Shi-Gang Sun,^b Wen-Bin Cai^{*a}

^aShanghai Key Laboratory of Molecular Catalysis and Innovative Materials,
Collaborative Innovation Centre for Energy Materials, Department of Chemistry,
Fudan University, Shanghai 200433, China

^bState Key Laboratory of Physical Chemistry of Solid Surfaces, Department of
Chemistry, College of Chemistry and Chemical Engineering, School of Energy
Research, Xiamen University, Xiamen 361005, China

^cCollege of Environmental and Chemical Engineering, Shanghai University of
Electric Power, Shanghai, 200090, China

Corresponding Author

* E-mail: wbc@fudan.edu.cn (WBC); zhouzy@xmu.edu.cn (ZYZ)

1. OCP-t profiles for surface dissociation on Pd electrode

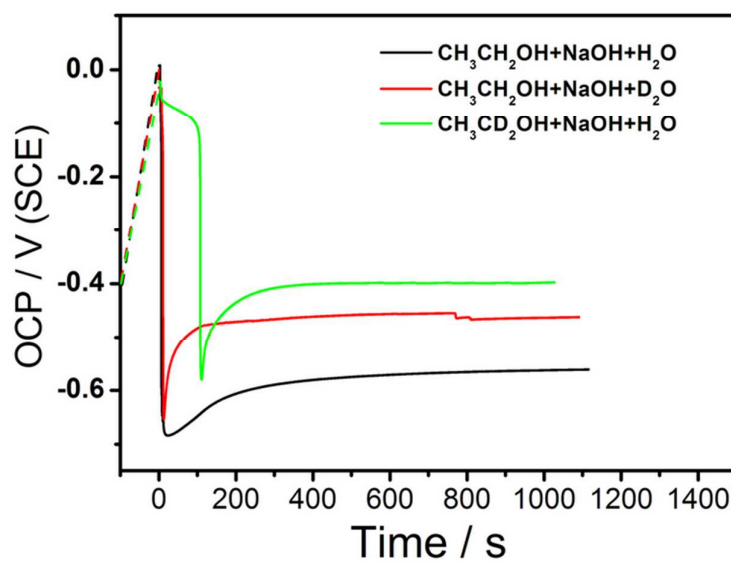


Figure S1. OCP-t profiles for $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CD}_2\text{OH}$ surface dissociation on Pd electrode in NaOH H_2O or D_2O solution

2. H-D kinetic isotope effect for EOR on Pd in NaOH solution

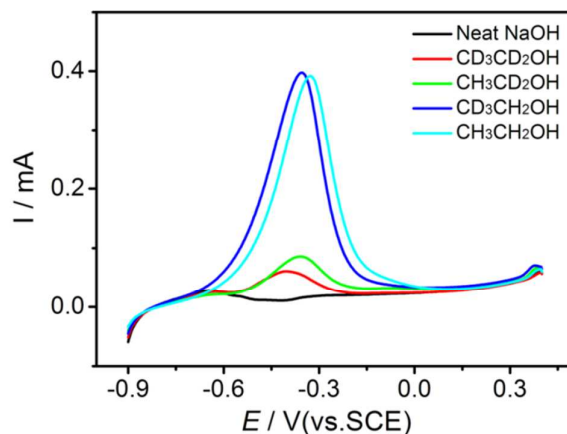


Figure S2. Cyclic voltammograms (CVs) of $\text{CH}_3\text{CH}_2\text{OH}$ and its deuteroderivatives ($\text{CD}_3\text{CD}_2\text{OH}$, $\text{CH}_3\text{CD}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{OH}$) on Pd electrode in 1 M NaOH solution containing 0.1 M alcohol at a scan rate of 50 mV s^{-1} .

To further understand the KIE of ethanol surface reaction, we compared the CVs between $\text{CH}_3\text{CH}_2\text{OH}$ and its different deuteroderivatives in 1 M NaOH solution. As shown in Figure S1, the onset oxidation potentials show no clear shift, but their peak currents (I_p) are obviously different. Namely, the I_p values for $\text{CD}_3\text{CD}_2\text{OH}$ and $\text{CH}_3\text{CD}_2\text{OH}$ are much smaller than those for $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CD}_3\text{CH}_2\text{OH}$. Specially, we used I_p values to estimate the kinetic constants according to the following equations:

$$K_1 = [I_p(\text{CH}_3\text{CH}_2\text{OH}) - I_p(\text{NaOH})] / [I_p(\text{CD}_3\text{CD}_2\text{OH}) - I_p(\text{NaOH})] \quad (1)$$

$$K_2 = [I_p(\text{CH}_3\text{CH}_2\text{OH}) - I_p(\text{NaOH})] / [I_p(\text{CH}_3\text{CD}_2\text{OH}) - I_p(\text{NaOH})] \quad (2)$$

$$K_3 = [I_p(\text{CH}_3\text{CH}_2\text{OH}) - I_p(\text{NaOH})] / [I_p(\text{CD}_3\text{CH}_2\text{OH}) - I_p(\text{NaOH})] \quad (3)$$

The calculation results are $K_1 = 7.64$, $K_2 = 5.24$, $K_3 = 0.99$, respectively. The result of $K_1 > K_2 \gg K_3$ indicates that the cleavage of $\alpha\text{-C-H}$ rather than $\beta\text{-C-H}$ plays an initial step for EOR at Pd electrode in alkaline media. Moreover, to some extent, it proves that adsorbed acetyl generated by $\alpha\text{-C-H}$ cleavage is the key intermediate for EOR. This will be detailed discussed in our other publications.

3. The band-fitting of ATR-SEIRA Spectra

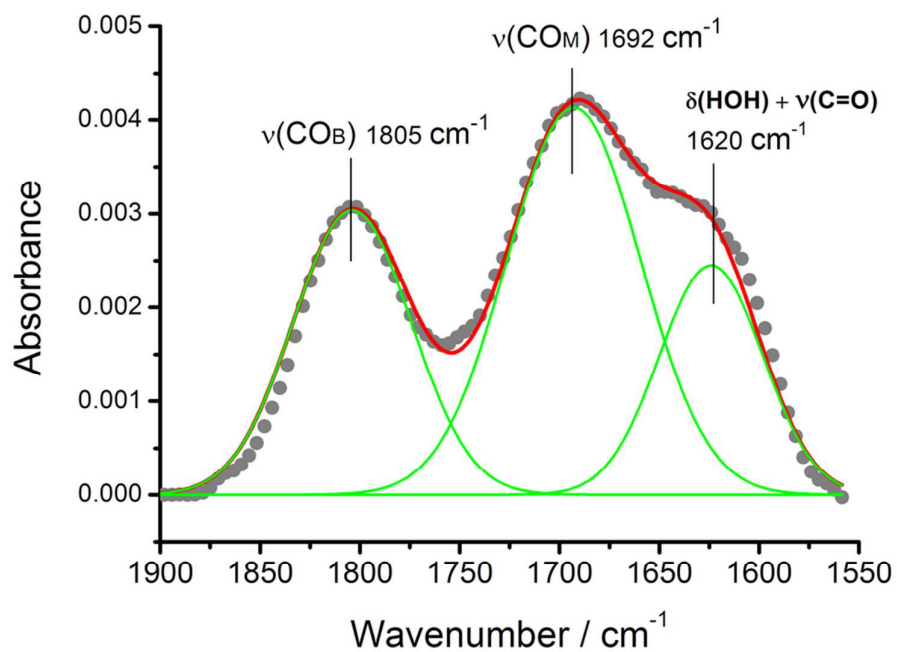


Figure S3. The Peak-fitting of ATR-SEIRA Spectra in Figure. 2B, taken the spectrum at -0.575 V (SCE) as example.