Supporting Information

Insight into C+O(OH) Reaction for Carbon Elimination on Different types of

CoNi(111) Surfaces: A DFT Study

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Rate constant calculations

In this study, the rate constants of C+O(OH) reaction involved in carbon elimination at different temperatures have been calculated to further understand the effect of reaction temperature on the kinetic of carbon elimination on Ni(111) and the alloyed CoNi(111) surfaces. Meanwhile, previous studies have reported that catalytic reforming of CH₄ with CO₂ is a highly endothermic reaction, which requires the operating temperatures of 800~1000 K to obtain the high equilibrium conversion of CH₄ and CO₂ to H₂ and CO, and to minimize the thermodynamic driving force for carbon deposition.¹ Therefore, on the basis of the harmonic Transition State Theory (TST),² the rate constants of the most favorable path of C+O(OH) reaction at the temperature of 800, 850, 900, 950 and 1000 K have been examined, respectively.

The rate constant can be obtained using the following formula:²

$$k = \frac{k_{\rm B}T}{h} \frac{q_{\rm TS}}{q_{\rm React}} \exp\left(-\frac{E_{\rm a}}{k_{\rm B}T}\right)$$
(1)

Here $k_{\rm B}$ is the Boltzmann constant, *h* is the Planck constant, *T* is the absolute temperature, $E_{\rm a}$ is the zero-point-corrected energy difference between the transition state and the co-adsorbed reactants. The partition functions (*q*) are calculated in the harmonic model in Eq.(2), where *v* is the vibrational frequency.

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$$q = \frac{1}{\sum_{i=1}^{Vibrations} 1 - \exp\left(-\frac{hv_{i}}{k_{\rm B}T}\right)}$$
(2)

The zero-point-corrected activation barriers (E_a) is determined from Eqs.(3) and (4):³

$$E_{\rm a} = (E_{\rm TS} - E_{\rm IS}) + \Delta ZPE_{\rm barrier}$$
(3)

where E_{TS} corresponds to the TS energy, E_{IS} refers to the reactant energy, and $\Delta ZPE_{\text{barrier}}$ refers to ZPE correction. For the co-adsorbed reactants, the reactant energy (E_{IS}) is calculated as the sum of individual BEs. ZPE correction for the activation barrier is determined from the equation below.

$$\Delta ZPE_{\text{barrier}} = \left(\sum_{i=1}^{V \text{ibrations}} \frac{hv_i}{2}\right)_{\text{TS}} - \left(\sum_{i=1}^{V \text{ibrations}} \frac{hv_i}{2}\right)_{\text{IS}}$$
(4)

According to these formulas as described above, the rate constants for C+O(OH) reaction have been calculated, and the corresponding results are listed in Table 3 in the main text.

References

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