

Supporting Information

Mechanistic Insights for Dry Reforming of Methane on Cu/Ni Bimetallic Catalysts: DFT-Assisted Microkinetic Analysis for Coke Resistance

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1. Computational Details

1.1. Exchange Correlation Energy Approximations

The approximation of the exchange-correlation functional is a primary concern for the accuracy of DFT [1]. Two exchange-correlation approximations are the Local Density Approximation (LDA) and Generalized Gradient Approximation GGA. In LDA, the exchange-correlation is approximated by considering the inhomogeneous electron gas as being locally homogeneous, thus applying the exchange-correlation hole of the homogeneous electron gas [2]. GGA approximation improves over LDA by taking into account the gradient of the density [3]. Multiple GGA functionals have been developed throughout time, and one popular choice is the Perdew-Burke-Ernzerhof (PBE) functional. Another GGA functional derived from PBE is the revised PBE functional suggested by Hammer et al. (RPBE) [4,5]. It is optimized for chemisorption, which is of unique importance for microkinetic modeling [4,5].

1.2. Energy Barriers with Nudged Elastic Band

Nudged Elastic Band (NEB) is a method of finding the minimum energy path (MEP) between an initial state and a final state, and NEB is also used to identify transition states. The initial and final atomic positions are determined to initialize the NEB calculation for adsorption configurations. The resulting atomic arrangements are called the images, and the distance between the images is described in a reaction coordinate. Structural optimization is performed for each image connected to another image by modifying the force component parallel to the MEP. The total force of each image, F , is decomposed into parallel ($F_{\parallel}$) and perpendicular components ($F_{\perp}$) as follows:

$$F = F_{\parallel} + F_{\perp} = -Kr + F_{\perp} \quad (1)$$

where K is the spring constant, r is the image position. Typically, the transition state cannot be found without releasing the highest energy image from all spring forces and reversing the actual parallel force component. As a result, the image climbs up the MEP to the actual transition state. This procedure is called the climbing image method.

1.3. Rate Constant Calculation

The temperature dependence of the rate k of one or another thermally activated process in solids or atomic clusters (diffusion, decomposition, isomerization, etc.) is often described by the harmonic approximation to transition state theory (hTST). It is typically used in studies of diffusion and reactions at the crystal or crystal surface. Accordingly, the rate constant $k^{\text{hTST}}(T)$ can be calculated as:

$$k^{\text{hTST}}(T) = A \exp(-E_a/K_B T) \quad (2)$$

where T is the temperature, K_B is the Boltzmann constant, E_a is the activation energy (the minimum energy required to transfer to the system to overcome the energy barrier of the corresponding reaction path), and A is the frequency coefficient with a dimension of s^{-1} [6,7]. The frequency factor A is calculated according to the Vineyard formula for N -atom clusters with zero values of the total momentum and the total angular momentum.

$$A = \frac{\prod_{i=1}^{3N-6} \nu_i}{\prod_{i=1}^{3N-6} \nu'_i} \quad (3)$$

where ν_i is the vibration eigenfrequency of the cluster in the state corresponding to the minimum of the potential energy (E_{pot}) for all $3N - 6$ normal modes of vibration for a non-linear molecule. ν'_i is the frequency of vibrations at the saddle point corresponding to the maximum of E_{pot} for one normal coordinate and the minimum for all the other coordinates [7]. Similarly, the zero-point energy correction, E_{ZPE} , can be calculated as [8]:

$$E_{\text{ZPE}} = \sum_i \frac{h\nu_i}{2} \quad (4)$$

where h is the Planck constant.

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