Supporting Information

Density Functional Theory Study of Edge-Induced Atomic Scale Structural Phase Transitions of MoS_2 Nanocrystals: Implications for High-Performance Catalyst

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Estimation of size limit for phase transition by gas molecules

To find the size limit of the MoS_2 nanocrystals, we analytically estimated the energy differences between H and T phases because it is difficult to directly perform DFT calculations for arbitrary large-sized nanocrystals. We first calculated total energy of the H and T phase MoS_2 nanocrystals with various size n = 3, 6, 8, and 10. For the next step, we estimated energy differences $\Delta E(n) = E_{\mathrm{T}}(n) - E_{\mathrm{H}}(n)$ of H and T phases considering CO and COS molecules that are involved in the phase change for each size n (Figure S1).

The energy difference between H and T phases can be divided into a portion of the basal plane and the edge. The energy difference in the basal plane is proportional to n^2 and the energy difference in the edge is proportional to n. Therefore, we can fit the energy difference into a quadratic polynomial of n and we can find n where $\Delta E(n) > 0$ (that is, when the H phase becomes more stable than the T phase) using the equation obtained through fitting. The results are $n \approx 11.15$ in the case of S-edge nanocrystal, and $n \approx 12.83$ in the case of Mo-edge nanocrystal. As a result, the size limit at which the T phase can exist are n = 11 for S-edge and n = 12 for Mo-edge nanocrystals.

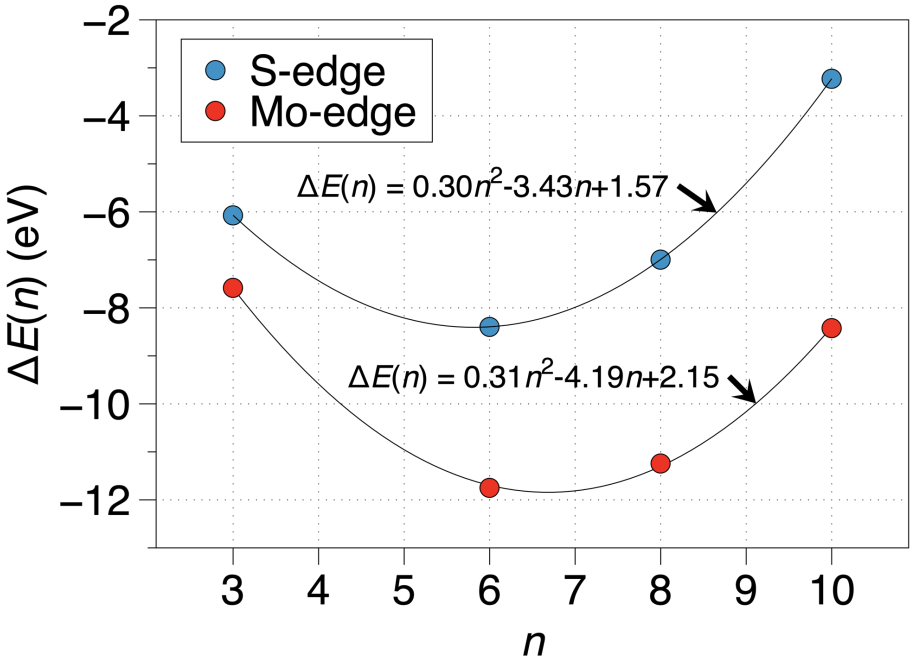

Figure S1. Energy differences $\boldsymbol{\Delta E(n)}$ between H and T phases for some cases. We calculated DFT total energy of S- and Mo-edge nanocrystals for the size of $n = 3, 6, 8$, and 10 and fitted energy differences between H and T phases into a quadratic equation of n. Then we obtained equations that represent relationship between size and energy difference of two phases. Using these equations, we found the size limit of the reaction mechanism proposed in the present report.