DFT Study of Edge-Induced Structural Phase Transitions of MoS_2 Nanocrystals

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Molybdenum disulfide (MoS_2) has attracted much attention as a material to replace the noble-metal-based hydrogen evolution reaction catalyst.[1] Polymorphism is an important factor in improving the catalytic performance of transition-metal dichalcogenides (TMDs) including MoS_2.[2] Several methods have been proposed to synthesize the 1T/1T′ phase with high catalytic efficiency, and a gas−solid reaction has recently been proposed as one of the alternative methods.[3] However, the atomic-scale reaction mechanism between gas molecules and MoS_2 has not been clarified. Here, we report a detailed atomic-scale mechanism of structural phase transition of MoS_2 nanocrystals under reaction with CO gas molecules using density functional theory calculations.[4] We confirm that the evaporation of S atoms at the edge is much faster than the evaporation at the basal plane of MoS_2 nanocrystals. It is found that the S evaporation at the edge induces the structural change from 2H to 1T/1T′ in the basal plane of nanocrystals. The structural change is also attributed to the chain reaction due to the sequential migration of S atoms to the octahedral sites, which is energetically favorable. The present results provide a guideline for the gas−solid reaction-based phase control of TMDs including MoS_2 to synthesize a high-performance catalyst.

References

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Figures

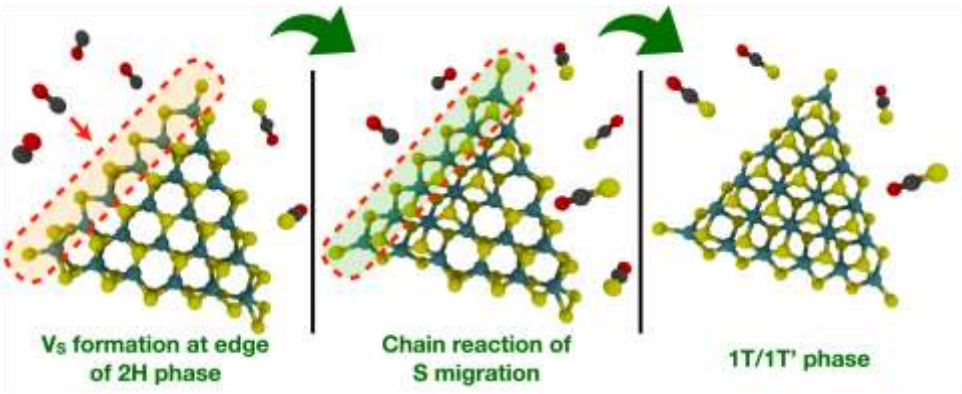

Figure 1: Schematic atomic models for the structural phase transition of MoS_2 nanocrystals by CO gas molecules.