Two-dimensional transition metal dichalcogenides as catalysts for organic reduction reactions: rationalizing activity trends

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Abstract

Two-dimensional transition metal dichalcogenides (2D TMDs), especially MoS_2, have arisen as attractive catalysts for the reduction of nitroarenes in the context of environmental remediation applications. This is due to their relative abundance, high surface area and tunable presence of structural defects (e.g., unsaturated metal sites at edges and chalcogen vacancies) acting as the active sites [1]. Here, the performance of 2D $MoSe_2$ nanosheets as a catalyst for nitroarene reduction (nitroanilines and nitrophenols) was investigated and found to be far higher than that of their MoS_2 counterpart. Analysis of the reduction kinetics for both TMDs suggested an enhanced nitroarene conversion rate at the active sites of the $MoSe_2$ nanosheets. This was interpreted to arise from a higher availability of reducing species (hydrides) in the latter, which in turn reflected the different reducibility of the active sites in the two TMDs. The different activity of the 2D $MoSe_2$ catalyst observed towards different structural isomers (e.g., 2-, 3- and 4-nitroaniline) were rationalized by density functional theory (DFT) calculations, which revealed that isomer selectivity relied on subtle differences in their adsorption at the active sites. DFT analysis also disclosed a feasible nitroarene reduction mechanism on 2D $MoSe_2$, involving active site passivation by oxygen from the nitro group and its reactivation by a reducing hydride. To facilitate their practical implementation, the bare $MoSe_2$ nanosheets were immobilized on polymer foam, affording their serial manipulation and reutilization for different consecutive catalytic cycles with no significant loss of activity. Overall, these results expand the scope of 2D TMDs as competitive catalysts for nitroarene reduction beyond MoS_2 and provide a rational framework to understand their catalytic mechanisms.

References

[1] Martínez-Jódar, A., Villar-Rodil, S., Salvadó, M. A., Carrasco, D. F., Pertierra, P., Recio, J. M., & Paredes, J. I., Applied Catalysis B: Environmental, 339 (2023), 123174.

Figures

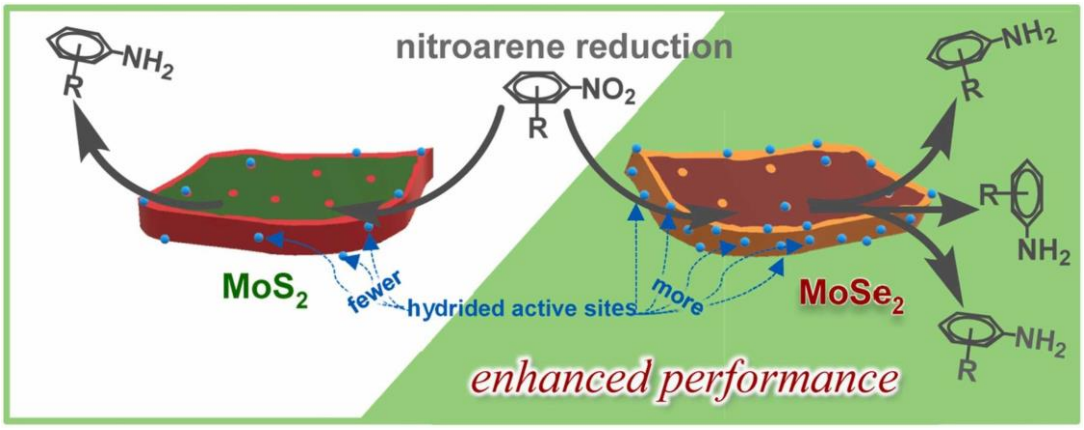

Figure 1: Representative scheme of catalytic reduction mechanism of nitroarenes using MoS_2 and $MoSe_2$ nanosheets as the catalyst.