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Refinerment of olefins via a periodic pi-conjugated network

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The purification of light olefins is essential in industrial utilization of from petrochemical feedstocks. The current technology of cryogenic distillation and its associated high energetic cost drives the research into alternative methods of purification. Transition metals that reversibly bind olefins are being studied to improve the energetic efficiency, but have several problems such as poisoning and deactivation. Beyond this, homogeneous catalysts present practical issues, such as separation or use of solvents, which are reduced by using related heterogeneous catalysts. In this work, we evaluate a 2D material recently synthesized by Kambe et al.,[1] with benzenehexathiol and Ni atoms in a 2:3 ratio, which was recently reported to coordinate ethylene.[2]

We have extended our previous computational work in molecular complexes[3,4,5] to the 2D system, using periodic boundary conditions (PBC) with a screened-hybrid DFT functional. In addition to those previously proposed, we include binding motifs both from the molecular analogues (e.g. coordination along the sulfur-nickel bond) and those arising from the periodicity (e.g. coordination between different nickel atoms). Relative energies of the coordination products and their formation pathways are compared to find the preferred mechanism. Different alkene coverage levels on the surface are used to evaluate the molecular efficiency of the material.

Reaction barriers and energies are similar to those obtained for molecular systems. Coordination is favored up to one ethylene per nickel atom. The extended material eases practical issues and weight efficiency improves. This is thusa promising candidate for an olefin purification catalyst.

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