DFT investigation of MoS_2 nanoclusters used as desulfurization catalysts

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Supported single layer MoS_2 is a long established catalyst used by the petroleum industry to remove sulfur from fossil fuels. It is believed the catalytic activity occurs at the edge of the MoS_2 nanoparticles. Support for this idea has been strengthened by recent atomic-scale images of MoS_2 nanoclusters which were obtained under working catalytic conditions by using scanning tunneling microscopy (STM). The images show that certain triangular shaped 'magic clusters' are formed, where the triangular shape is attributed to stabilization from excess sulfur at the cluster edges. In the first part of the talk we will present the results from density functional theory (DFT) calculations on $Mo_{10}S_x$ clusters with x =12, 18, 24, 30 and 36 and describe how we have used these calculations to predict STM images for these different clusters. The MoS_2 nanoclusters can in principle be formed with either a sulfided Mo edge or a sulfided S edge. In the experimental work, the STM image assigned to a $Mo_{10}S_{30}$ cluster (originally assigned to $Mo_{10}S_{24}$) was described as having fully sulfided S edges, whereas the larger MoS_2 nanoclusters were assigned to have fully sulfided Mo edges. In contrast our calculations, using both our predicted STM images and the cluster DFT total energies, suggest that the experimental STM images still correspond to nanoclusters where the sulfided Mo edges are still more stable than cluster with sulfided S edges. In the second part of the talk we will describe recent calculations on Mo_3S_x, with x = 0 to 12 which simulate possible desulfurization pathways for organosulfur compounds.