Zinc dialkyldithiophosphates adsorption and dissociation on ferrous substrates: An ab initio study

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KEYWORDS
Lubricant additives, Tribofilms and 3rd bodies, Modelling in tribology, ZDDP

ABSTRACT
Zinc dialkyldithiophosphates (ZDDPs) have been commonly used as anti-wear additives in the automotive industry for the past 80 years. Despite their widespread use, a general agreement on their primary functioning mechanism is still lacking. The morphology and composition of the ZDDPs phosphate-based tribofilm, which is essential for its lubricant functioning, have been widely studied experimentally[1-3]. However, the formation process and the relevant driving forces are still largely debated. In particular, it is unclear whether the stress-induced molecular dissociation occurs in the bulk oil or on the substrate. In this work, we employ ab initio density functional theory simulations to compare ZDDP fragmentation in vacuum and over a reactive substrate, considering the effects of surface oxidation on the dissociation path. To do so, we developed a computational protocol to study the effects of shear stress on molecules. Our results show that the molecular dissociation is endothermic in the absence of a supporting substrate, while in the presence of an iron substrate, it becomes highly energetically favoured. Moreover, the presence of the substrate changes the reaction path, inducing the detachment of organophosphorus units from Zn-S ones. At the same time, surface oxidation reduces the molecule–substrate interaction. These findings provide valuable insights into the early stages of the formation of phosphate-based tribofilms[4].

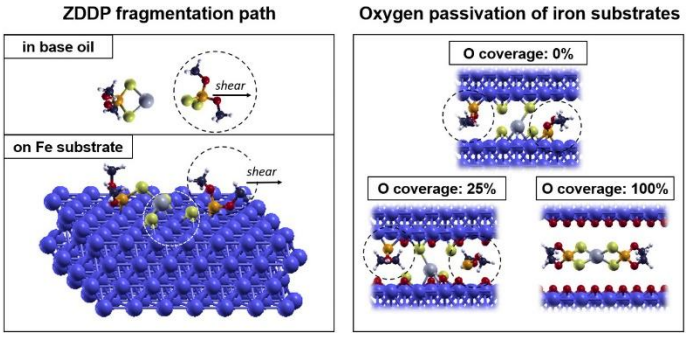

Fig.1 ZDDP adsorption and dissociation on ferrous substrates.

ACKNOWLEDGMENTS

These results are part of the "Advancing Solid Interface and Lubricants by First Principles Material Design (SLIDE)" project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant agreement No. 865633).

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