Coupling experimental and numerical approaches to study adsorption mechanism of stearic acid on iron based surfaces

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1. Introduction

Organic friction modifiers (OFMs) have been used for many years in metallic contacts to reduce friction under mild conditions. The interest for such friction modifiers strongly increased in the recent years because of environmental regulations ask for slightly hazardous lubricant additives. It is proposed here to revisit adsorption and friction behavior of fatty acids by coupling experimental and computational chemistry approaches to better understand their mechanism of action and optimize their performance.

2. Methodology

In this paper stearic acid was studied as an OFM and was used as pure additive or blended at 1\% w in PAO4 synthetic base oil. The surfaces of interest used were iron-based materials (including pure iron and iron oxides) as they can be encountered in a steel/steel contact under mild or severe friction conditions. Adsorption and friction properties of such systems were studied experimentally by friction tests, XPS and PM-IRRAS surface analyses. Computational chemistry (UA-QCMD) was also used to study the adsorption kinetics. In the following, adsorption experiments, computational chemistry simulations and friction test are detailed.

Adsorption experiments of stearic acid vapor on the different surfaces were carried out in an environmentally controlled chamber and this was followed by in-situ XPS analyses of the surfaces. Stearic acid vapor was generated in the adsorption chamber in presence of the different substrates at different adsorption time (10 min to 2 hours).

Computational chemistry study was also performed to investigate the in vacuo interaction of stearic acid molecules with the different substrate (pure iron, Fe\textsubscript{3}O\textsubscript{4}, and FeOOH). An ultra-accelerated quantum chemical MD (UA-QCMD) simulator has been used in order to deal with chemical reaction dynamics for large complex systems [1]. Different models have been built starting with one single molecule up to self-assembled monolayer (SAM) on iron based surfaces at 50 °C. Eventually, friction experiments were carried out with a cylinder-on-flat reciprocating tribometer using AISI 52100 steel cylinders and flats.

3. Results and discussion

Adsorption experiments

\textit{In-situ} XPS analyses results, especially the position of the C1s peak contribution from the carboxylic group, show differences depending on the nature of surfaces.

Computational chemistry

As said before, different models have been built starting with one single molecule up to self-assembled monolayer (SAM) on iron based surfaces at 50 °C. We found differences in adsorption energy (physisorption or chemisorption) depending on the kind of surface (pure iron, Fe\textsubscript{3}O\textsubscript{4} and FeOOH) and regarding the presence of one single molecule or a SAM.

Friction tests

After the tribological tests, PM-IRRAS analyses were conducted on the tribofilms. Results show the presence of stearic acid in the wear track as well as carboxylate forms.

The experimental and simulation results for both adsorption and friction experiments will be discussed for a better understanding of stearic acid complex interactions with iron-based surfaces.