In situ Spectroscopic Characterization of Carbonaceous Deposit Formation in Diesel Engines: Nucleation and Growth

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Developments in the automotive industry to reduce emissions and fuel consumption has resulted in diesel injectors with micro-scale clearances that are highly susceptible to blockages due to deposit formation. Even small amounts of deposit can cause the moving parts of the injector to stick, leading to increased harmful emissions and reduced engine efficiency and power. The effort to reduce the impact of a diesel engine over its operating life relies on a thorough understanding of the interaction between the fuel and the engine surfaces. An understanding of the deposition mechanism enables the design of fuel formulations and additive packages that minimize, and ideally prevent, deposit formation.

In the work model diesel and model surfaces have been used to simulate deposit formation. These deposits have been extensively characterised with SIMS, XPS and SEM, and are found to consist of oxidised carbonaceous species. Systematic in-house studies showed the key role of iron in deposit formation: 1) limited deposition was observed on non-metallic surfaces; 2) a significant increase in the mass and the oxygen content of the model diesel is observed in the presence of iron.

Here we have carried out *in situ* XAS at Beamline I20 at Diamond Light Source and at Beamline MRCAT at the Advanced Photon Source (APS) to investigate the reactive role of iron during deposition. Due the challenge of understanding the interface and attaining solely surface-sensitive information, we used a single layer and a stack of thin films in fluorescence and transmission modes respectively. We developed a cell and a flow-rig to facilitate *in situ* XANES measurements of the changes at the interface at 200^{o}C as a function of film thickness. This set up also facilitated the study of interfacial kinetics with model diesel components: hexadecane, 1-methyl naphthalene and decalin.

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