

# Influence of Ligand Modifications on Catalyst Positioning in Supported Ionic Liquid Phase (SILP) Systems

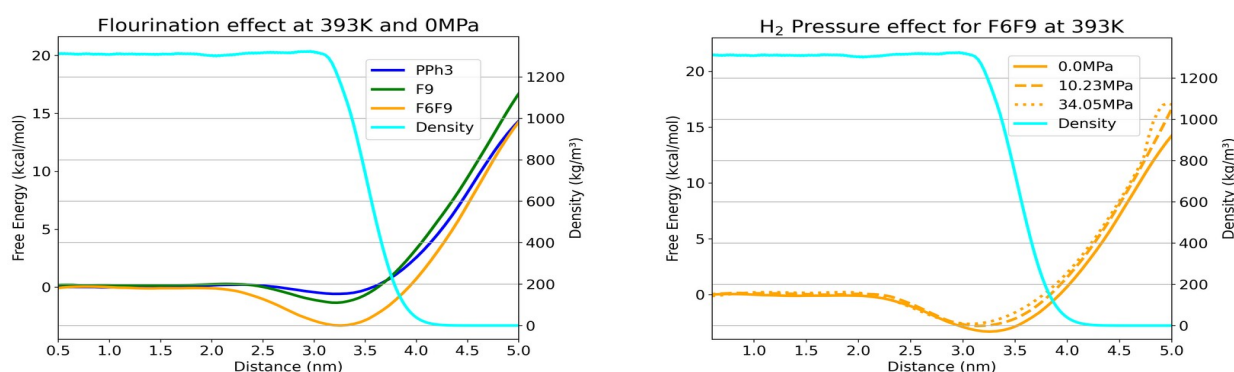
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Supported Ionic Liquid Phase (SILP) catalysis utilizes a thin film of ionic liquid (IL) containing a homogeneous catalyst and is widely applied in hydrogen-involved catalytic systems. Understanding the interfacial behavior of the catalyst under reaction conditions is crucial for optimizing performance. Our study investigates how ligand modifications and interface dynamics influence catalyst positioning at IL/gas interfaces in the presence of a reactant gas. We selected Wilkinson's catalyst, a well-known hydrogenation catalyst, and H<sub>2</sub>, the key reactant in hydrogenation reactions, for this study.

We performed Molecular Dynamics (MD) simulations on mixtures of [BMIM][NTf<sub>2</sub>] and Wilkinson's catalyst (represented as PPh<sub>3</sub>) or its two derivatives fluorinated to different degrees (represented as F9 and F6F9) under pressurized H<sub>2</sub> across varying temperatures and pressures. The influence of H<sub>2</sub> on interfacial properties, and the impact of fluorinated ligands in enhancing catalyst surface affinity were examined. To further explore the local solvation environment of the catalyst, we conducted a 3D density analysis of atomic distributions within a defined spatial region around Rhodium (Rh), revealing preferential accumulation of ions of the IL and gas molecules.



Our findings indicate mild surface enrichment of H<sub>2</sub>, which decreases with increasing pressure and temperature, mirroring trends in IL surface tension.<sup>1,2</sup> The increase in the degree of fluorination of the ligands enhances the surface affinity of the catalyst, as evidenced by computed potential of mean force (PMF) profiles depicted above, and the corresponding free energy gain upon surface accumulation. Specifically, the fluorinated catalyst (F6F9) exhibited a four-fold increase in surface affinity compared to its unmodified counterpart, Wilkinson's catalyst (PPh<sub>3</sub>). To understand the molecular origin of this design, we analyze in detail the non-homogeneous environment of the catalysts in the bulk liquid and at the interface. The obtained insights highlight how interfacial modifications and ligand engineering can enhance the surface enrichment of the catalyst, potentially improving the performance of SILP catalytic systems.

[1] Zhai, Z., et al., International Journal of Hydrogen Energy, **2024**, 72, 1091-1104,

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[2] Zhai, Z., et al., Journal of Molecular Liquids, **2023**, 386, 122388

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