Water co-adsorption in ultrathin films of ionic liquids on Pt(111)

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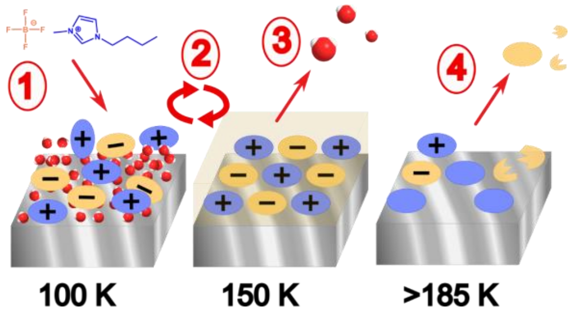
Ionic liquids (ILs) are key components of the Solid Catalyst with Ionic Liquid Layer (SCILL) concept, where thin IL films on heterogeneous catalysts enhance selectivity in various catalytic reactions. Since water is a common and often unavoidable contaminant in ILs, understanding its influence on the structure and adsorption behavior of IL films at metal interfaces is essential for the rational design of SCILL systems.

We investigated the influence of pre-adsorbed water (D_2O) on the adsorption, orientation, and thermal behavior of four ionic liquids (ILs) — the hydrophilic $[C_4C_1Im][BF_4]$ and $[C_2C_1Im][TfO]$, and the hydrophobic $[C_3CNC_1Im][Tf_2N]$ and $[C_1C_1Im][Tf_2N]$ — on Pt(111) using angle-resolved X-ray photoelectron spectroscopy.[1-2] The ILs were deposited at ~100 K onto clean Pt(111) or onto crystalline (CI) or amorphous (ASW) D_2O films, and analyzed at various temperatures. At 100 K, the IL predominantly adsorbs on top of the water layer. Upon heating to ~130 K, an exchange process occurs in which the IL replaces interfacial water from the Pt surface into the second layer, as deduced from a reduced water desorption temperature by ~9 K. By ~150 K, water has fully desorbed, yielding a pure IL layer with a characteristic checkerboard arrangement of alternating anions and flat-lying cations. Further heating shows that this layer behaves identical to IL films directly deposited on clean Pt(111): Above ~185-270 K (IL dependent), the IL decomposes stepwise, with anion-derived fragments fully desorbing until ~400-500 K whereas most cation-derived products remain as carbonaceous residues up to at least ~550-800 K. The comparable water co-adsorption behaviour observed for all ILs shows that neither the hydrophilicity nor the nitrile-functionalisation in $[C_3CNC_1Im][Tf_2N]$ significantly influences adsorption characteristics or thermal stability.



Scheme 1: Thermal behaviour of water and $[C_4C_1Im][BF_4]$ co-adsorption on Pt(111) (taken from [2])

REFERENCES

1. T. Talwar, H. P. Steinruck, F. Maier, "Water Co-Adsorption in Ultrathin Films of Ionic Liquids on Pt(111)" *ChemistryOpen* **2025**, e202500571.
2. T. Talwar, H. P. Steinruck, F. Maier, "The interplay of water and the hydrophilic ionic liquid $[C_4C_1Im][BF_4]$ on Pt(111)" Submitted to *Surface Science* **2026**