

Adsorption and structure formation of the carbonyl-functionalized ionic liquid [5-oxo-C₆C₁Im][NTf₂] on Au(111): A combined IRAS, STM, DFT, and MD study

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The coating of heterogeneous catalysts with ionic liquids allows for the precise tuning of catalytic activity and selectivity. The fundamentals of Solid Catalysts with Ionic Liquid Layers (SCILL) have been intensively studied recently. The next step of this research is the investigation of the interaction between functionalized ionic liquids (IL) and atomically defined model systems.

In this study, we investigated the carbonyl-functionalized ionic liquid [5-oxo-C₆C₁Im][NTf₂] on an Au(111) surface. To examine the adsorption, interaction, and thermal behavior of the IL on the surface, we deposited the IL by physical vapor deposition (PVD) under ultrahigh vacuum (UHV) conditions. We monitored the adsorption and thermal evolution of the IL in-situ using time-resolved and temperature-programmed infrared reflection absorption spectroscopy (TR-IRAS / TP-IRAS) and scanning tunneling microscopy (STM). Furthermore, we performed density functional theory (DFT) calculations and molecular dynamics (MD) simulations to support the interpretation of the experimental data.

We observed that the weakly bound multilayer of [5-oxo-C₆C₁Im][NTf₂] is stable on Au(111) up to ~380 K under UHV conditions. The more strongly bound monolayer desorbs at ~500 K. [5-oxo-C₆C₁Im][NTf₂] preferentially adsorbs at the step edges and on the elbows of the herringbone reconstruction of Au(111). At temperatures below 200 K, the IL adsorbs in the form of small islands. With increasing temperature, the IL becomes more mobile on the surface, forming larger islands instead of the smaller, scattered aggregates. At low coverage, the carbonyl group of the [5-oxo-C₆C₁Im]⁺ cation is oriented in parallel with the Au(111) surface. This suggests that the alkyl chain of the cation is in contact with the surface. As the coverage increases, the alkyl chain detaches from the surface and aligns towards the vacuum.