

Real-time view on deprotonation induced phase transitions of self-assembled 4,4'-biphenyl dicarboxylic acid on Ag(001) surfaces

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Deprotonation of carboxylic groups on surfaces is one of the basic reaction steps leading to the formation of new molecular surface phases. In this contribution, we describe the kinetics of the deprotonation-induced irreversible phase transitions of 4,4'-biphenyl dicarboxylic acid (BDA) on Ag(001) surface under ultra-high vacuum conditions. The real-time view by low energy electron microscopy (LEEM) complemented with low energy electron diffraction (LEED), STM, non-contact AFM, and XPS, supported by DFT and kinetic Monte Carlo simulations, provides new insights on the deprotonation reaction. In this way, we were able to reveal and describe a set of molecular phases consisting of a different mixture of BDA molecules with a distinct level of deprotonation. We will highlight the initial α to β phase transformation and distinct behavior of the full molecular layer.

The phase transformation is shown to exhibit a wide variety of phenomena that are well described by a general growth-conversion-growth (GCG) model. Here, the two-dimensional gas of ad molecules has a dual role: it mediates mass transport between the molecular islands and hosts a slow deprotonation reaction. Further, we show that our observations are consistent with burst nucleation kinetics and point out the significant role of surface step-edges in this process. In the full molecular layer, the mass transport via on-surface diffusion in the full monolayer is hindered, and phases different than for monolayer are observed.