Grand canonical Monte Carlo simulation of Fe-terephtalate ordering on Cu(100)

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Surface confined metal-organic networks (SMON) have been attracting much attention in recent years, since they represent a unique type of two-dimensional materials that have new magnetic, electronic and catalytic properties [1,2]. The structure of SMONs is similar to the metalloenzymes. Therefore, it can be also considered as models to study the chemical reactivity in living matter [3]. SMON structure is determined by a subtle balance between molecule-molecule interactions, metal-molecule interactions, and molecule-surface interactions. In this regard, the structure and properties of SMON are much richer comparing to 3D MOFs. For the same reason, the structure and physicochemical properties of SMON are extremely difficult to control. It requires a detailed understanding of the mechanisms and driving forces of the SMON self-assembly.

Here we report a detailed lattice model of terephthalic acid (TPA) and iron ordering on Cu (100) surface under ultra-high vacuum conditions, taking into account multiple interactions in the adlayer: carboxylate-Fe coordination, hydrogen bonding and surface mediated interactions. We have calculated the phase diagram of the adlayer using the ground state analysis and grand canonical Monte Carlo simulation as implemented in the SUSMOST code [4]. It has been established that one type of the ladder structures distinguished on scanning tunneling microscopy images is a metastable state and not a phase in the thermodynamic sense. We have found two new metal-organic structures, which are missed in earlier studies, but apparently formed in the TPA-Fe/Cu(100) adsorption layer. The first one is characterized by the lowest density of the monolayer. Another phase is formed at high densities, even higher than the densest structure observed experimentally.

Also we have revealed that long-range interactions between Fe-Fe and TPA-Fe are needed to reproduce most of the structures found experimentally [2].

We believe that our theoretical investigation insights will be helpful for understanding the self-assembly of metal-organic networks on metal surfaces and stimulate further experimental work.

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References

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